



## Equilibrium and kinetic studies – adsorption of phenol using a de-oiled cake of *Jatropha* sp.

Subramanyam Busetty<sup>a,\*</sup>, Ashutosh Das<sup>b</sup>

<sup>a</sup>School of Civil Engineering, SASTRA Deemed University, Thanjavur, Tamil Nadu, India, emails: subramanyamjy@gmail.com/  
subramanyam@civil.sastra.edu (S. Busetty)

<sup>b</sup>Director, Centre for Research and Development, PRIST Deemed University, Tamil Nadu, India, email: enviroondas@gmail.com (A. Das)

Received 31 March 2020; Accepted 15 September 2020

---

### ABSTRACT

The adsorption of phenol by de-oiled cake of *Jatropha* has been studied to determine its potential usage as an adsorbent in the treatment of aqueous phenolic solution. In the current research, the influence of several process parameters (namely, pH, initial phenol concentration, and amount of adsorbent) has been explored to maximize the phenol-sorption potential of *Jatropha* de-oiled cake. The optimum phenol uptake was estimated for initial concentration (100 mg/L), solution pH (6.0), adsorbent dosage (6 g/L), and contact time (6.5 h). The suitability of isotherms amongst various bi-parametric isotherm models is, found to be in the following order: Langmuir and modified Langmuir-1 > Temkin > Freundlich > D–R. The equilibrium adsorption capacity (mg/g) was found to be 12.5 and 14.3 mg/g (for second-order model) and the rate of the adsorption process was found to be better described using the pseudo-second-order kinetic model. The adsorption process was found to be essentially chemisorption.

*Keywords:* Adsorption; De-oiled cake; Isotherms; Equilibrium and kinetic models

---

### 1. Introduction

Phenolic pollutants are especially obnoxious in effluents from a wide range of chemical industries, viz. coal refineries, resin paint, dyeing, textile, wood, petrochemical, pulp mill, and so forth [1]. Phenol and its vapors are known to be scarring to the eyes, the skin, and the respiratory tract [2]. In fact, frequent or continued skin contact with phenol could lead to dermatitis or even second and third-degree burns. Besides, the breathing of phenol vapor may also result in lung infections. Phenol has also been reported to cause injury to the central nervous system and heart, thereby causing seizures, and even coma [3]. Recurring acquaintance of the phenol has been found to damage the liver and kidneys, as well. Phenol is a crucial raw material and/or product of pharmaceutical and associated industries and is disreputable for its high toxicity

and difficulty in biodegradability at high concentrations. Phenol and phenolic compounds are highly carcinogenic. They have been classified as priority pollutants by the US Environmental Protection Agency (EPA) because of their high toxicity even at low concentrations. The Food and Drug Administration (FDA) and Indian Standard Drinking water have determined that the phenol concentration in bottled drinking water should not exceed 0.001 mg/L [2].

Several researchers have investigated different types of adsorbents to remove pollutants from the wastewater and aqueous solutions. The adsorption of phenol onto chitin, a naturally occurring material, showed highest phenol adsorption capacity to be 21.5 mg g<sup>-1</sup> (for 300 mg dm<sup>-3</sup> initial phenol concentration, at pH 1.0 and a temperature of 40°C). The Langmuir and Freundlich adsorption models are most widely used to express the sorption phenomenon of the sorbates [4]. A study on the use of chemical activated

---

\* Corresponding author.

carbon (from tea residue) for removal of phenol has reported a maximum phenol adsorption capacity of  $320 \text{ mg g}^{-1}$ , with the kinetics of the system being in agreement with Elovich kinetic model and isotherm with the Langmuir and BET models [5]. Djilani et al. [6] used activated carbon prepared from apricot stones at different adsorbent dosage ranged from 2–12 g/L and estimated a range of 35%–90% removal efficiency of chloro-phenol from its aqueous solution.

Garba et al. [7] evaluated the adsorption capacity of activated carbon from oil palm shell has been produced by chemical activation using  $\text{K}_2\text{CO}_3$  for the removal of phenol in a fixed-bed column. The column studies were carried out at pH of 6.5 and the maximum sorption capacity of the carbon for phenol was estimated to be  $238.12 \text{ mg/g}$ . Tural et al. [8] studied the chitosan-coated magnetite nanoparticles as a biosorbent for the removal of phenol, 2-CPh, and 4-CPh from aqueous solutions which revealed the adsorption following pseudo-second-order reaction and equilibrium experiments obeying Freundlich isotherm model.

Alam Khan and Ahmad [9], on the study of Langmuir and Freundlich isotherms, observed that the monolayer adsorption capacity of polyaniline Sn(IV) silico-phosphate (PTSP) for phenol adsorption was found to be 3.76, 5.58, and  $2.82 \mu\text{g g}^{-1}$  at  $30^\circ\text{C}$ ,  $40^\circ\text{C}$ , and  $50^\circ\text{C}$ , respectively (at optimum pH 3–5). Das et al. [10] proved that the de-oiled cake of *Jatropha* was found to have good adsorption characteristics, and exploited in the elimination of dyes from aqueous solutions. The feasibility of *Jatropha* de-oiled cake as an adsorbent for the removal of reactive red dye from aqueous solutions have been explored. Based on their analysis of different equilibrium isotherms, Redlich–Peterson, and Sip isotherm models were found to be the best representatives for reactive red dye sorption on the *Jatropha* de-oiled cake adsorbent. Nacke et al. [11] focused on to evaluate the removal of Cd(II) from water using three biosorbent originated from the biomass of *Jatropha*. The adsorption process had been evaluated by the studies of kinetics, isotherms, and thermodynamics. The maximum adsorption capacity (Langmuir isotherm model) for bark, endosperm, and bark + endosperm of *Jatropha* was estimated to be 29.665, 19.562, and  $34.674 \text{ mg g}^{-1}$ , respectively. Thus, indicating predominating chemisorption as monolayers. Ge et al. [12] in their effort toward utilization of various forms and compositions of organically-modified magadiite (MAG–CTAB–KH550) to enhance the adsorption capacity to remove phenol, used two parametric isotherms to explain the experimental data. They observed that Langmuir isotherm seemed to be a better fit compared to Freundlich isotherm, which, in turn, describe the chemical adsorption mechanisms and explain the phenol adsorption (by both MAG and MAG–CTAB–KH550). Li et al. [13], studied the adsorption of phenol and 2-nitrophenol on to a biochar in single and binary systems at different temperature ( $298\text{--}328 \text{ K}$ ) at pH 5. They observed adsorption capacities of phenol to be significantly reduced from single to binary systems, compared to those obtained for 2-nitrophenol. Nidhi et al. [14], compared the adsorption efficiencies of the magnetic activated carbon synthesized from cauliflower waste at two different temperatures ( $250^\circ\text{C}$  and  $500^\circ\text{C}$ ) for PNP removal by the two adsorbents and reported that the adsorbent pyrolyzed at the higher temperature was

found to be more efficient. The adsorption of PNP by both the adsorbents was supported by the Freundlich isotherm with the  $R^2$  value 0.98 and 0.94 for CAC-250 and CAC-500, respectively. The adsorption of both phenol and PNP was best fitted with the pseudo-second-order kinetics.

The novelty of the studies caters to the various selection of the adsorbent for dephenolation of an aqueous phenolated solution, that is, a de-oiled cake from *Jatropha* seeds. In fact, production of biofuels from the *Jatropha*, which is techno economically attractive solution, by, under least maintenance and wide adaptability to varying litho-climatic regimes and low cost (yet high yield) characteristics of the plant. Besides the de-oiled cake, which is a by-product of oil extortion from *Jatropha*, is known to be toxic, preventing animal fodder, and composting pathways of utilization, thereby letting adsorption as the only option. The present aims are to study the adsorption capacity of *Jatropha* de-oiled cake as an adsorbent for removal phenol from its aqueous solutions.

## 2. Materials and methods

### 2.1. Selection and characterization of adsorbent

The de-oiled cake used for the present study was obtained from cold-pressing of *Jatropha* seeds, using conventional oil mill. The de-oiled cakes, thus collected, was allowed to undergo a pretreatment process of boiling with water for removing dust, oil remains, and other impurities from the raw de-oiled cake. The hydro-extracted residue, thus obtained, was dried in a hot air oven (48 h;  $100^\circ\text{C}$ ), followed by grinding, sieving (100–635 SIEVE NO ASTM E11-87), and obtained sample were preserved (without adding preservatives) in dark brown coloured air-tight container (to prevent photo oxidant) for further analysis and experimentations.

The detailed elemental analysis of *Jatropha* de-oiled cake used for adsorption (before and after adsorption) was presented in Table 1. The surface morphology of the *Jatropha* de-oiled cake, used for study, was observed using the scanning electron microscopy (SEM) (Fig. 1). It can be seen from the micrographs that the external surface of the chemically acidulated (using 1 N HCl) adsorbent is full of alterations and striations with cavities. Also, it can be seen that some scatterings are found on the surface of the adsorbents (as well as, to some extent, some blockage of the entry of pores).

### 2.2. Analysis of adsorbate

Phenol ( $\text{C}_6\text{H}_5\text{OH}$ ) of analytical reagent (AR) grade was used for making phenol stock solution and stored in a dark glass container (to prevent photo-oxidation) for further experiments. UV/vis spectrophotometer (Hach model DR6000, Made in USA) is used to estimate the phenol concentrations during the experiment, using a characteristic peak wavelength of 270 nm.

### 2.3. Adsorption batch studies

The adsorption experiments were conducted in the laboratory at ambient temperature ( $30^\circ\text{C} \pm 2^\circ\text{C}$ ) to know the upshot of different experimental factors (namely, adsorbent

Table 1  
Elemental analysis of *Jatropha* deoiled cake (before and after adsorption)

Element	<i>Jatropha</i> deoiled cake before adsorption		<i>Jatropha</i> deoiled cake after adsorption		Enrichment as a result of adsorption	
	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%
C	59.67	67.03	75.04	81.48	15.37	14.45
N	0	0	3.12	2.9	3.12	2.9
O	37.81	31.88	15.51	12.65	-22.3	-19.23
Na	0.09	0.05	2.78	1.58	2.69	1.53
Mg	0.48	0.26	0.07	0.04	-0.41	-0.22
Al	0.05	0.03	0	0	-0.05	-0.03
Si	0.15	0.07	0.26	0.12	0.11	0.05
P	0.5	0.22	1.13	0.48	0.63	0.26
S	0.2	0.09	0.09	0.04	-0.11	-0.05
Cl	0.11	0.04	1.77	0.65	1.66	0.61
K	0.55	0.19	0.1	0.03	-0.45	-0.16
Ca	0.39	0.13	0.13	0.04	-0.26	-0.09

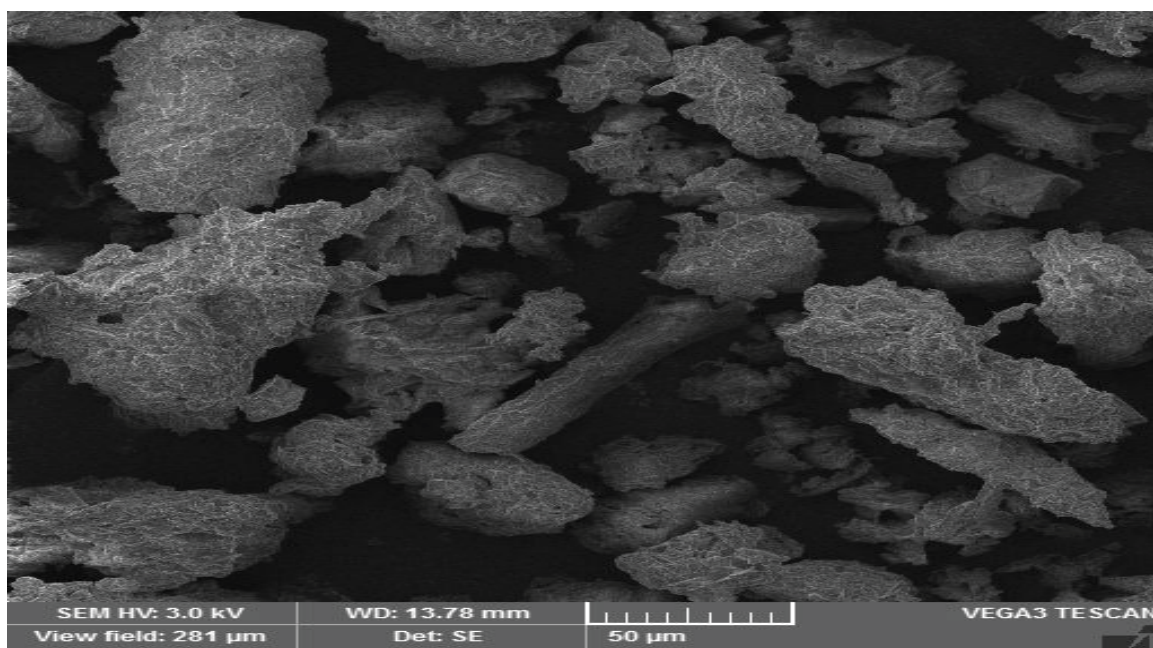


Fig. 1. Surface morphology of the raw *Jatropha* before adsorption.

dosage, pH, contact time, and initial concentration) upon phenol-sorption potential of *Jatropha* de-oiled cake. The effect of pH on adsorption of phenol by *Jatropha* de-oiled cake was conducted in the range of pH 2 to pH 12, the solution pH attuned by using 0.1 M solutions of two, to reagents, viz. HCl and NaOH. For each experimental setup, 100 mL of known concentration of aqueous phenol were taken in 250 mL conical flask and different dosages of adsorbents were added and kept in a shaker. The samples, being equilibrated for 24 h, were filtered using Whatman filter paper and analysed for equilibrium phenol concentrations. The quantity of phenol taken up by the adsorbent was premeditated by, means of the standard equation:

$$Q = \frac{(C_0 - C_e)}{M} V \quad (1)$$

where  $C_0$  is the initial phenol concentration (mg/L),  $C_e$  is the equilibrium of phenol concentration in the solution (mg/L),  $V$  is the adsorbate volume (L), and  $M$  is the mass of adsorbent (g).

#### 2.4. Kinetics and isotherm studies

Batch kinetic studies were conducted at the optimum dosage of adsorbent by adding various dosages of adsorbate, until

the equilibrium condition has arrived. To study the order of kinetics, different kinetics models were applied (*viz.*- pseudo-first-order and pseudo-second-order) and to explain the equilibrium adsorption of phenol, three bi-parametric isotherm models (namely, Freundlich, Langmuir, Tempkin, Dubinin–Radushkevich, and Langmuir modified) and three tri-parametric isotherm models (namely, Redlich–Peterson, Langmuir Freundlich, and Sip isotherms) were used.

#### 2.4.1. Langmuir isotherm model [15]

This model explains the number of active sites that are available for adsorption. The general Langmuir's isotherm and described as follows:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (2)$$

#### 2.4.2. Freundlich model [15]

The Freundlich model is explained the multilayer sorption. The Freundlich isotherm model is an empirical equation employed for modeling the adsorption on heterogeneous surfaces. Freundlich isotherm and described as follows:

$$q_e = K_F C_e^{1/n} \quad (3)$$

where  $K_F$  is a constant, indicating the relative adsorption capacity of the adsorbent ( $\text{mg}^{1-(1/n)} \text{L}^{1/n}/\text{g}$ ) and  $n$  is a constant, representing the intensity of adsorption.

#### 2.4.3. Dubinin–Radushkevich isotherm [16]

Dubinin–Radushkevich (D–R) isotherm is used to estimate the typical porosity along with seeming adsorption free energy. Hence, to evaluate these parameters, the Dubinin–Radushkevich isotherm is presented and described as follows:

$$q_e = K_{\text{DR}} \exp \left[ b \left( RT \ln \left( 1 + \frac{1}{C_e} \right) \right)^2 \right] \quad (4)$$

where  $q_e$  is the equilibrium adsorption capacity (mg/g),  $C_e$  is the equilibrium concentration (mg/L),  $K_{\text{DR}}$  is the free energy of adsorption, and  $b$  is the Dubinin–Radushkevich isotherm constant of adsorption.

#### 2.4.4. Modified Langmuir – 1 [17]

$$q_e = \frac{b T^{-n} C_e}{1 + b C_e} \quad (5)$$

where  $q_e$  and  $C_e$  explains their usual connotations as given above;  $T$  is the temperature in Kelvin; and  $b$  is the free energy constant as, L/mg.

#### 2.4.5. Temkin model [18]

Temkin isotherm model considers the interactions of adsorbate on adsorption isotherms and recommended that

the heat of adsorption energy present in the molecules of the layer would decrease linearly with coverage. Temkin isotherm described in the following form:

$$Q_e = \frac{RT}{b} (\ln A C_e) \quad (6)$$

where  $q_e$  is the equilibrium adsorption capacity (mg/g),  $C_e$  is the equilibrium concentration (mg/L),  $A$  and  $b$  are the isotherm constants.

#### 2.4.6. Redlich–Peterson [19]

The Redlich–Peterson equation and described as follows:

$$q_e = \frac{K_{\text{RP}} C_e}{\left[ 1 + \alpha_{\text{RP}} C_e^\beta \right]} \quad (7)$$

where  $K_{\text{RP}}$  and  $\alpha_{\text{RP}}$  are Redlich–Peterson constants of isotherm and “ $\beta$ ” is the exponent normally lies between 0 and 1.

#### 2.4.7. Langmuir–Freundlich isotherm [20]

$$q_e = \frac{q_{\text{mLF}} (K_{\text{LF}} C_e)^{\text{mLF}}}{1 + (K_{\text{LF}} C_e)^{\text{mLF}}} \quad (8)$$

where  $q_e$  is the adsorbed amount at equilibrium (mg/g),  $q_{\text{mLF}}$  is the Langmuir–Freundlich maximum adsorption capacity (mg/g),  $C_e$  is the equilibrium concentration (mg/L),  $K_{\text{LF}}$  is the equilibrium constant for a heterogeneous surface, and  $\text{mLF}$  is Langmuir Freundlich heterogeneity parameter, which lies between 1 and 0. The Langmuir–Freundlich isotherm model at low adsorbate concentrations remarkably gets reduced to Freundlich isotherm and hence does not follow Henry's law. At high adsorbate concentrations, this model behaves as monolayer adsorption and follows Langmuir isotherm characteristics.

#### 2.4.8. Sip isotherm

The equation of Sip isotherm model is presented and described as follows:

$$q_e = \frac{(K_s C_e)^\beta}{\left[ 1 + (\alpha_s C_e)^\beta \right]} \quad (9)$$

where  $K_s$  (L/g) and  $(\alpha_s C_e)^\beta$  are the Sips isotherm constants and “ $\beta$ ” is the exponent which lies between 1 and 0.

Fig. 4 presents the two-parameter isotherms models fit for the along with experimental data. Table 2 shows the coefficients of isotherm coefficients along with corresponding correlation coefficient, standard deviations of the residuals for all sorbent–sorbate system.

### 2.5. Surface area

A known quantity of adsorbent (oven-dried at 105°C and desiccated) was transferred to a conical flask and allowed for 24 h to be in contact with distilled water to estimate the

Table 2  
Details of two parameter isotherm constants for phenol adsorption by *Jatropha* deoiled cake

Langmuir	Freundlich	Modified Langmuir-1	D-R	Temkin
$B$ 28.970	$K_f$ 3.143	$B$ 0.029	$K_{DR}$ 20.550	$B$ 0.3642
$q_m$ 0.0286	$n$ 2.342	$N$ -0.589	$B$ 60.120	$A$ 0.2321
$R^2$ 0.9841	$R^2$ 0.983	$R^2$ 0.984	$R^2$ 0.913	$R^2$ 0.9839
$SS^a$ 0.6995	$SS^a$ 0.730	$SS^a$ 0.699	$SS^a$ 3.841	$SS^a$ 0.7092

<sup>a</sup>Absolute sum of square

quantity of water adsorbed [21]. Following equation is used to find the surface area of the adsorbent sample:

$$S = 3612\omega \quad (10)$$

where  $S$  is the specific surface area,  $m^2/g$ ;  $\omega$  is the equilibrium moisture content in "g" water adsorbed per "g" of de-oiled *Jatropha*.

### 2.6. Thermodynamic studies

The thermodynamics studies were conducted at 20°C–40°C to study the effect of temperature on phenol adsorption. The adsorption of phenol by the de-oiled *Jatropha* was carried out in batch studies, by maintaining constant temperatures by thermostatic water bath (separately at 20°C, 30°C, and 40°C) for 6.5 h, which was found to be the optimum time for adsorption equilibrium.

## 3. Results and discussion

### 3.1. Effect of pH

The batch system factors, such as agitation speed, equilibrium time, initial adsorbate concentration, and adsorbent dosages were kept constant, only the pH of the adsorbate was varied to estimate the optimum pH for adsorption (which was found to be 6.0) (Fig. 2). The lower phenol adsorption by de-oiled *Jatropha* cake at high pH condition may be a due decrease in the capacity of the un-ionized species like halogenated organic compounds and, increase of the ionized species. The effect of adsorption capacity can be explained by the separation of functional groups on the surface of the adsorbent, which subsequently leads to a change in the kinetic reactions and equilibrium conditions of adsorption process [22]. However, lower pH, because, of the generation of more cations, on the surface of the adsorbent, is likely to result in relatively higher adsorption capacity [23]. Hence, the rest of the experiments were carried out "at pH ~6."

### 3.2. Effect of adsorbent dosage

The effect of adsorbent dosage (50–1,000 mg/100 mL) on the adsorption of phenol by de-oiled cake is, presented in Fig. 3, which reveals an, increase in the removal of phenol, associated with increasing the adsorbents dosage (up to 6 g/L). This increase of the adsorption capacity with increasing dosage of adsorbent may be ascribed to availability

of more significant number of surface sites for retaining the adsorbate molecules. However, a further increase in adsorbent dosage (beyond 6 g/L) is likely to have caused a reduction of the removal efficiency because of the need of more force to push the molecules into the active sites. In fact, the amount of phenol adsorbed is found to be maximum only at optimum adsorbent dosage, which may be due to the availability of enough driving force per unit surface area of adsorbent at this equilibrium condition [23].

### 3.3. Determination of equilibrium time

#### 3.3.1. Effect of initial phenol concentration and contact time

The obtained experimental results disclose fast uptake of phenol at the initial stages of the contact period, a steady

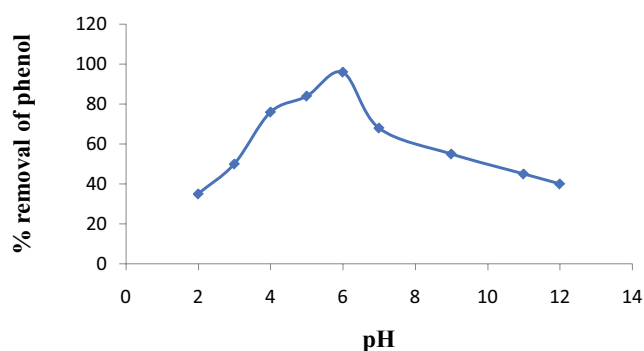


Fig. 2. Effect of adsorbent dosage on phenol adsorption.

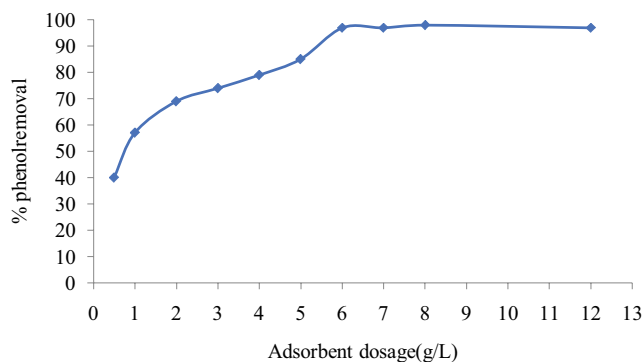


Fig. 3. Effect of adsorbent dosage on phenol adsorption.

slow down as it approached equilibrium, with a constant rate of adsorption at the intermediate stages (Fig. 4). The total adsorption carried out with different initial concentrations ( $C_0$ ) was found to be almost in the same order at contact time of 6.5 h, in comparison to contact time of 24 h and hence 6.5 h was considered as equilibrium time for present adsorption studies. Thus, the batch study results disclose that the rate of phenol adsorption seems to be fast at the early phase, and subsequently, slower as approaches the equilibrium stage, which may be because of more availability of free surface sites at the initial stage of adsorption and progressively reduced availability of sites due to increasing in repulsive forces between the adsorbent and adsorbate [24].

3.4. Isotherm studies

Several adsorption isotherms models have been used to study the nature of adsorption as well as optimizing the design of an adsorption process. The most used isotherms are Langmuir and Freundlich isotherms. The Langmuir isotherm equation [10], follows Henry’s law at low concentrations and is valid for homogeneous surfaces. Freundlich isotherm equation [7] is highly suitable for heterogeneous surfaces, over restricted ranges of concentrations. Besides, the Redlich–Peterson equation [7] is widely used as a compromise between Langmuir and Freundlich isotherms and is mostly used to represent solute adsorption data on heterogeneous surfaces. Sip model [8] equation follow Freundlich isotherm at lower solute concentration and follows Langmuir isotherm at higher solute concentration.

It is essential to find the best isotherm model for improved understanding of the mechanism and to compute the isotherm models achieved for the de-oiled *Jatropha* adsorption experiments. For this purpose, Langmuir, Freundlich, Dubinin–Radushkevich (D–R), modified Langmuir-1, Temkin, Langmuir–Freundlich, Redlich–Peterson, and Sip isotherm models were used and assessed against experimental data for the goodness of fit. Fig. 5 (comparison of two parametric isotherm models) and Fig. 6 (comparison of three parametric isotherm models) represents the assessment of the experimental and calculated amount of phenol adsorbed on to the de-oiled *Jatropha*.

The principles for selection of the isotherm model were based on respective correlation coefficient and absolute

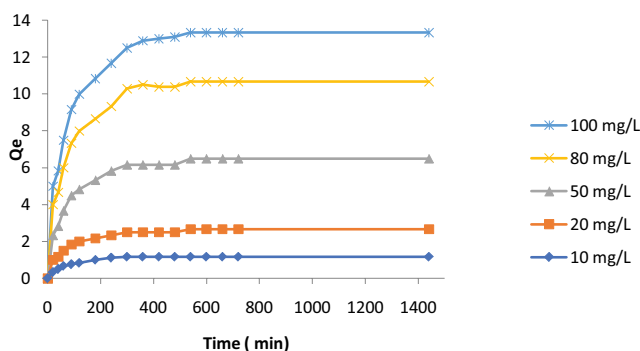


Fig. 4. Effect of initial concentration of phenol adsorption.

sum of squares. Based on these values, the Langmuir and modified Langmuir-1 isotherm model could reasonably fit the data, with a correlation coefficient 0.984 and absolute sum of squares 0.699. In addition to two parametric isotherm models, to further minimize the error and therefore to get the best fit, three parametric models were tried and assessed. All the three-parametric models’ isotherm models (Langmuir–Freundlich, Redlich–Peterson, and Sip isotherm) were observed to fit the experimental data and are remarkably similar. The fitted parameter values for all the isotherms used are shown in Tables 2 and 3.

3.4.1. Forecasting best two and three-parameter model isotherm

The Langmuir isotherm model signifies the monolayer coverage for the sorbate–sorbsent system. The above isotherm model measures the maximum adsorption capacity agreeing with the monolayer exposure. To describe potential multilayer adsorption and non-linear energy sharing for the adsorption sites, the Freundlich isotherm was used. The Freundlich constants’ and “ $n$ ” are the measures of adsorption capacity and intensity of adsorption. Numerous investigators had modified the classical Langmuir equation by reorganizing the constants without changing the degree of freedom [25–27]. The modified Langmuir model-1 accounts for temperature variability and heterogeneity of the adsorbent of the system, respectively [28]. In the present study, modified Langmuir-1 isotherm model was used to know the sorption capacity of the system. The negative value  $n$  indicates that phenol adsorption could be supportive at high temperature.

The D–R isotherm is especially suitable for gaseous phase adsorption as well as solid–liquid phase adsorption [29].

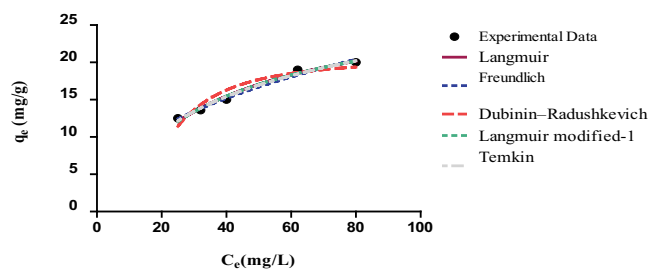


Fig. 5. Two-parameter isotherm models.

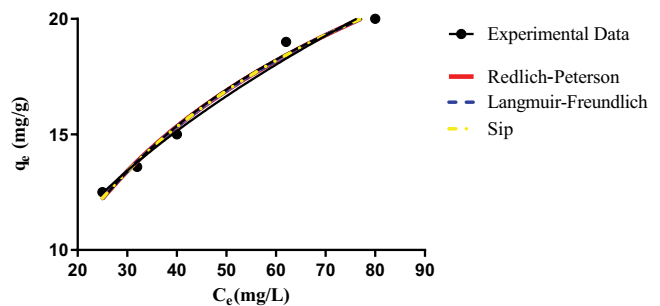


Fig. 6. Three-parameter isotherm models.

The Temkin isotherm model is based on uniform distribution of binding energies up to a certain extent [29,30].

The two-parameter isotherms models fit experimental data fairly well (Fig. 5). The output shows the Temkin characteristic curves to be closer to the Langmuir, Freundlich, and modified Langmuir-1 curve. However, these provide no improvement over the Langmuir, Freundlich, and modified Langmuir-1 isotherm model, which are mathematically reasonably simple, yet widely applicable.

In comparison to the five non-linearized two parametric isotherm models, for sorbate–sorbent used in this study, it is identified that the Langmuir and modified Langmuir-1 isotherm models showed higher value of correlation coefficient ( $R^2 = 0.9841$ ) and lower value of standard deviation residual values ( $S_e = 0.6995$ ) than that of the other two bi-parameter isotherm models (Table 2). The order of suitability of isotherms is as follows: Langmuir and modified Langmuir-1 > Temkin > Freundlich > D–R.

### 3.4.2. Three parameter models

By using three-parameter isotherm models, viz., Sip, Langmuir–Freundlich, and Redlich–Peterson, the adsorption capacity of the sorbate–sorbent system can be predicted. The three-parameter models explain the adsorption capacity,  $q_m$ , as intrinsic function of the equilibrium concentration and are empirical. Fig. 6 reveals that the models seem to fit well with the sorbate–sorbent system. The model constant values along with the respective correlation coefficient and standard deviation residual values of the sorbent–sorbate system presented in Table 3. In the present research study, the Redlich–Peterson isotherm model is found to fit the experimental data better than all the two-parameter isotherm models studied (Fig. 4). In many cases, the applicability of the Redlich–Peterson isotherm model is studied with only two parameter isotherm models viz., Langmuir and Freundlich isotherm models (Table 3).

The Langmuir–Freundlich isotherm model is derived based on functional characteristics of both Langmuir and Freundlich isotherms. The values of the maximum adsorption capacity obtained for the sorbate–sorbent system using the Langmuir–Freundlich isotherm model are higher than those calculated by the Langmuir and Freundlich isotherm models, as shown in Table 2. The model which fits for the Langmuir–Freundlich and Sip isotherm models along with experimental study data, are presented in Fig. 4.

The exponent  $\beta$ -value is found to be in the range of 0.7387 for sorbate–sorbent system studied herewith. From

the results, it may be inferred that the adsorption is likely to be multilayer in nature (note, the experimental data obeys Freundlich isotherm model).

### 3.5. Kinetic studies

To control the process efficiency in the adsorption, process several kinetic models like pseudo-first-order and pseudo-second-order models have been studied.

#### 3.5.1. Pseudo-first-order model

The pseudo-first-order rate equation designated by:

$$\frac{d q_t}{d t} = K_t (q_e - q_t) \tag{11}$$

where  $K_t$  is the pseudo-first-order rate constant. By applying integration, the conditions,  $q_t = 0$ ; at  $t = 0$  and at  $t = t$ ,  $q_t = q_t$  becomes, the model study for various concentration is presented in the Fig. 5.

#### 3.5.2. Pseudo-second-order model

The pseudo-second-order kinetic model is expressed as follows:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{12}$$

where  $k_2$  is the second-order rate constant (g/mg min).

By plotting of “ $t/q$ ” vs. “ $t$ ,” the values of  $k_2$  and  $q_e$  were calculated from the standard linear equations intercept and slope. The model study for various concentrations is presented in Fig. 7.

#### 3.5.3. Kinetic results analysis

To examine the mechanism of sorption and potential rate-controlling steps, kinetic models have been used to validate experimental data. The kinetics of adsorption of de-oiled cake *Jatropha* have been studied by applying first-order and second-order kinetic equations. The best-fit model was, selected based on the linear regression correlation coefficient,  $R^2$ , values. In the case of non-porous media and porous media, the adsorption mechanism can be

Table 3  
Details of three parameter isotherm constants for *Jatropha* deoiled cake

Redlich–Peterson	Langmuir–Freundlich model	Sip
$K_{RP}$ 1.042	$q_m$ 39.5	$q_m$ 39.5
ALP 0.069	$K$ 0.014	$K$ 0.0137
BET 0.752	$M$ 0.739	$B$ 0.739
$R^2$ 0.986	$R^2$ 0.986	$R^2$ 0.986
SS 0.659	SS 0.624	SS 0.624

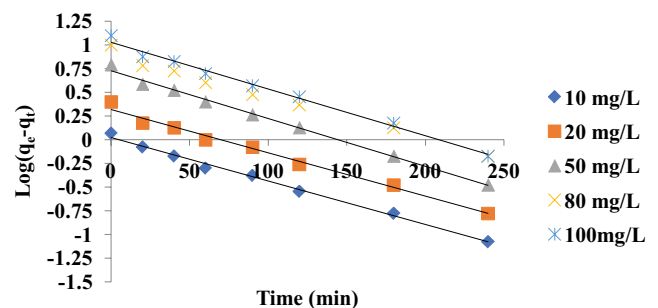


Fig. 7. Pseudo-first-order kinetic model.

Table 4  
Adsorption kinetic rate model constants for *Jatropha* deoiled cake (temperature 30°C ± 2°C at pH ~6)

Initial concentration	Experimental	Pseudo-first-order		Calculated	Pseudo-second-order			Calculated
$C_0$ (mg/L)	$q_e$ (mg/g)	$K_1$	$R^2$	$q_e$ (mg/g)	$K_2$	$h$	$R^2$	$q_e$ (mg/g)
10	1.1667	0.01197	0.9737	4.0551	0.0091	0.019	0.9945	1.4468
20	2.5	0.01059	0.9798	1.9994	0.0069	0.0563	0.9948	2.8596
50	6.1667	0.01129	0.9846	5.2156	0.0026	0.1316	0.9954	7.1582
80	10	0.01059	0.9798	7.9965	0.0017	0.2252	0.9948	11.4417
100	12.5	0.01059	0.9798	9.9954	0.0014	0.2815	0.9948	14.3062

Table 5  
Thermodynamics parameters

Adsorbent	Temperature (K)	$\Delta G^\circ$ J/mol	$\Delta H^\circ$ J/mol	$\Delta S^\circ$ J/mol/K
De-oiled <i>Jatropha</i>	293	-76.85	-36.63	1.05
	303	-79.65		
	313	-82.27		

either boundary layer diffusion (external mass transfer) or intra-particle diffusion [31]. Lagergren model was applied to study the first and second-order kinetics. The rate constants  $K_1$  and  $K_2$  were determined from the slope of the plot as shown in Fig. 6 and the results are presented in Table 4. The statistical analysis was carried out to obtain the best kinetic model.  $Q_{exp}$  values from pseudo-first-order shows striking difference in comparison with that obtained from pseudo-second-order and the pseudo-second-order reaction is found to be favorable. Hence, it is the rate-limiting step.

#### 3.5.4. Effect of temperature in the adsorption process

The influence of temperature on adsorption study involves the mass transfer, chemical, and energy changes. The negative values of  $\Delta G^\circ$  indicate that the adsorption of phenol on to the adsorbents is spontaneous as shown in Table 5. The negative value of  $\Delta H^\circ$  of phenol with de-oiled *Jatropha* proves that the adsorption is exothermic. The positive value of  $\Delta S^\circ$  indicates the increased randomness at the adsorbate/adsorbent interface during the adsorption process that the process is highly reversible.

#### 3.5.5. Effect of adsorption on the chemical composition of the de-oiled cake of *Jatropha*

The variation of the chemical composition of the adsorbent studied (both in terms of weight % and atomic %) was nearly in terms of enrichment of carbon and removal of oxygen, more than 15%. Probably this is because of partial chemisorption in the system (by oxidation of carbonaceous matrix of the adsorbent by the phenol, in the process of adsorption). The rest of the parameters are found to vary marginally (less than 5%). However, the extent of the chemisorption is very low, as revealed by high  $p$ -value obtained by paired  $t$ -test (~0.5 for two-tailed and ~1 for one-tailed tests).

## 4. Conclusions

The batch studies carried out to evaluate adsorption capacities of the de-oiled cake of *Jatropha* for phenol removal revealed that this adsorbent was found to show high adsorption efficiency (above 96%) at room temperature (30°C ± 2°C). The optimized dosage required for adsorption was found to be 6 g/L. The optimized contact times for all the adsorbents (*Jatropha* de-oiled cake) was found to be 390 min (on average). On analysis of the sorbate-sorbent systems, the higher parameter models are found to enhanced options for their modeling in comparison to lower parameter models. The kinetic reaction study reveals that the adsorption was found to support pseudo-second-order reaction for given adsorbent, which indicates that this model follows rate-limiting step. The overall change in chemical composition in the adsorbent due to adsorption was statistically not significant, as revealed by paired  $t$ -test, thus indicating the adsorption to be primarily physisorption. The present study is clear demonstration of the potential for agro-residue as real robust adsorbents.

## References

- [1] S.M. Abdoli, D. Bastani, H. Bargozi, Adsorption of phenol compounds by nano-porous silica aerogel, *Int. J. Sci. Technol.*, 22 (2015) 992–1000.
- [2] ATSDR, Toxicological Profile for Phenol, Agency for Toxic Substances and Disease Registry, U.S. Department of Health and Human Services, Atlanta, GA, 1998.
- [3] Documentation of the Threshold Limit Values and Biological Exposure Indices, 7th ed., American Conference of Governmental Industrial Hygienists, 2019.
- [4] Y. Arzu Dursun, Ç. Seda Kalayci, Equilibrium, kinetic and thermodynamic studies on the adsorption of phenol onto chitin, *J. Hazard. Mater.*, 123 (2005) 151–157.
- [5] J. Tao, P. Huo, Z. Fu, J. Zhang, Z. Yang, D. Zhang, Characterization and phenol adsorption performance of activated carbon prepared from tea residue by NaOH activation, *Environ. Technol.*, 40 (2017) 171–181.



- [6] C. Djilani, R. Zaghdoudi, F. Djazi, B. Boucekima, A. Lallam, A. Modarressi, M. Rogalski, Adsorption of dyes on activated carbon prepared from apricot stones and commercial activated carbon, *J. Taiwan Inst. Chem. Eng.*, 53 (2015) 112–121.
- [7] A. Garba, N.S. Nasri, H. Basri, R. Ismail, Z. Abdul Majid, D. Usman Hamza, J. Mohammed, Adsorptive removal of phenol from aqueous solution on a modified palm shell-based carbon: fixed-bed adsorption studies, *Desal. Water Treat.*, 57 (2016) 29488–29499.
- [8] B. Tural, E. Ertaş, S. Tural, Removal of phenolic pollutants from aqueous solutions by a simple magnetic separation, *Desal. Water Treat.*, 57 (2016) 26153–26164.
- [9] M. Alam Khan, A. Ahmad, Kinetics and thermodynamic studies of phenol adsorption on nanocomposite, *Desal. Water Treat.*, 57 (2016) 11255–11265.
- [10] A. Das, B. Subramanyam, G. Mukesh, B. Ram Kiran, K. Sudharshan, K. Ravi Kumar, Alternative usage of edible de-oiled cake for decolonization of Reactive Red dye, *Desal. Water Treat.*, 53 (2015) 2720–2726.
- [11] H. Nacke, A.C. Gonçalves, G.F. Coelho, Removal of Cd(II) from water using the waste of *Jatropha* fruit (*Jatropha curcas* L.), *Appl. Water Sci.*, 7 (2017) 3207–3222.
- [12] M. Ge, X. Wang, M. Du, G. Liang, G. Hu, J.A. S.M, Adsorption analyses of phenol from aqueous solutions using magadiite modified with organo-functional groups: kinetic and equilibrium studies, *Materials*, 12 (2019), doi: 10.3390/ma12010096.
- [13] Z. Li, L. Sellaoui, G.L. Dotto, A. Bonilla-Petriciolet, A.B. Lamine, Understanding the adsorption mechanism of phenol and 2-nitrophenol on a biopolymer-based biochar in single and binary systems via advanced modeling analysis, *Chem. Eng. J.*, 371 (2018) 1–16.
- [14] Y. Nidhi, M. Dhruv Narayan, R. Shalu, S. Jiwan, Adsorption and equilibrium studies of phenol and para-nitrophenol by magnetic activated carbon, 25 synthesised from cauliflower waste, *Environ. Eng. Res.*, 25 (2020) 742–752.
- [15] O. Cooney David, *Adsorption Design for Wastewater Treatment*, Lewis Publishers, CRC Press LLC, Boca Raton, FL, 1999.
- [16] J.M. Akhtar, S.M. Hasany, M.I. Bhangar, S. Iqbal, Low cost sorbents for the removal of methyl parathion pesticide from aqueous solutions, *Chemosphere*, 66 (2007) 1829–1838.
- [17] R.T. Yang, J. Doong, Gas separation by pressure swing adsorption: a pore diffusion model for bulk separation, *AIChE J.*, 31 (1985) 1829–1842.
- [18] C. Aharoni, F.C. Tompkins, Kinetics of Adsorption and Desorption and the Elovich Equation, D.D. Eley, H. Pines, P.B. Weisz, Eds., *Advance in Catalysis and Related Subjects*, Academic Press, New York, NY, 1970, pp. 1–49.
- [19] J.M.Y. Kim, K. Jae Park, B. Tuncer Edil, Sorption of organic compounds in the aqueous phase onto tire rubber, *J. Environ. Eng.*, 123 (1997) 827–835.
- [20] R. Sip, On the structure of a catalyst surface, *J. Chem. Phys.*, 16 (1948) 490–495 (as reference in the Hamdaouia and Naffrechouxl).
- [21] A. Sridharan, G.V. Rao, Surface area determination of clays, *Geotech. Eng.*, 3 (1972) 127–132 (as reference in the Developments in Geotechnical Engineering, 66, by T.S. Nagaraj, 1993).
- [22] F. Asaad Hassan, H. Elhadidly, Production of activated carbons from waste carpets and its applications in methylene blue adsorption: kinetic and thermodynamic studies, *J. Chem. Eng.*, 5 (2017) 955–963.
- [23] M. Radika, K. Palanivelu, Adsorptive removal of chlorophenols from aqueous solution by low cost adsorbents—kinetics and isotherm analysis, *J. Hazard. Mater.*, B, 138 (2006) 116–124.
- [24] A. Gunay, B. Ersoy, S. Dikmen, A. Evcin, Investigation of equilibrium, kinetic, thermodynamic and mechanism of Basic Blue 16 adsorption by montmorillonitic clay, *Adsorption*, 19 (2013) 757–768.
- [25] M. Gaulke, V. Guschin, S. Knapp, S. Pappert, W. Eckl, A unified kinetic model for adsorption and desorption - applied to water on zeolite, *Microporous Mesoporous Mater.*, 233 (2016) 39–44.
- [26] M.C. Tsai, S.S. Wang, R. Yang, Pore diffusion model for cyclic separation: temperature swing separation of hydrogen and methane at elevated pressures, *AIChE J.*, 29 (1983) 966–975.
- [27] V.V. Goud, K. Mohanty, M.S. Rao, N.S. Jayakumar, Phenol removal from aqueous solutions using tamarind nutshell activated carbon: batch and column study, *Chem. Eng. Technol.*, 28 (2005) 814–821.
- [28] J.A. O'Brien, A.L. Myers, Physical adsorption of gases on heterogeneous surfaces series expansion of isotherms using central moments of the adsorption energy distribution, *J. Chem. Soc., Faraday Trans.*, 80 (1984) 1467–1477.
- [29] N.S. Maurya, A.K. Mittal, Immobilisation of the dead fungal biomass for the treatment of coloured wastewater, *Environ. Eng. Manage. J.*, 5 (2006) 189–202.
- [30] R.D. Johnson, F.H. Arnold, The Temkin isotherm describes heterogeneous protein adsorption, *Biochim. Biophys. Acta*, 1247 (1995) 293–297.
- [31] C.N. Mohamed, M. Borhane, S. Mongi, Investigation of the sorption mechanisms of metal-complexed dye onto *Posidoniaoceanica* (L.) fibres through kinetic modelling analysis, *Biores. Technol.*, 99 (2008) 5582–5589.