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Validation of Flory-Huggins Model for Phenol Adsorption by Parthenium Hysterophorus in A Batch System

Zakia Latif[1], Aliya Fazal[2], Muhammad Aziz Choudhary[1], Zahoor Ahmad[1], Muhammad Aslam Mirza[1]

[1] Department of Chemistry, Mirpur University of Science& Technology (MUST), Mirpur,10250 AJ&K, Pakistan
[2] National centre for physics, Quaid-e-Azam University campus, Islamabad, 44000 Pakistan,

ABSTRACT

Parthenium hysterophorus weed powder was studied as adsorbent for phenol adsorption from its aqueous standardized solution. The adsorption of pollutant was found improving with an increase of biomass dosage and contact time. The intraparticle diffusion of phenol onto adsorbent surface was identified to be the rate limiting step. Linear form of Flory-Huggins model revealed preeminence to Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich due to highest value of R^2. The remediation process was figured out as a physisorption rather than a chemical one based on value of E (0.21KJ/mol). Active sites of sorbent surface identified by FT-IR were oxygen containing functional groups. Recent study proposes cost effective utilization of toxic allergent for treatment of toxic waste.

Keywords: Adsorption; Kinetic; Equilibrium; Active sites

1. Introduction

Against the principles of sustainable development, unrestrained industrial practices resulted undesirable rich levels of injurious and toxic substances in the environmental media. Industrial waste matter is often polluted with different compounds such as: metallic element, pendent solids, and dissolved organic compounds[1]. Among these xenobiotic phenol treatment is explored due to its release from major material and pharmaceutical industries, petrochemical industries, petroleum refineries, coal gasification operations, textiles, iron, steel, pulp and paper, plastic, rubber, and pesticides[2,3]. Phenol contaminated water remediation is necessary before discharge into natural water because they are classified as hazardous wastes and some are known or suspected as carcinogens. Environmental Protection Agency (EPA) has set a limit of phenol 0.1 mg/L in wastewater and 0.001 mg/L in potable water by The World Health Organization (WHO).

The existing problem of organic contaminant is resistance to decompose organically, opposes the self-purification capabilities of the rivers as well as remediation in conventional wastewater treatment plants[4]. Among the physicochemical processes that have proved useful for phenol treatment adsorption is particularly important due to its sludge free neat operation, economical, handiness of wide range of adsorbents and complete dismissal of phenols from wastewaters. Many agricultural wastes have been employed as adsorbent for the removal of phenol includes coconut shell[5], sawdust[6], apricot stone shell[7], sugarcane bagasse[8], peanut husk[9], coir pith and rice husk[10]. Present study is about use of Parthenium hysterophorous as adsorbent for remediation of phenol. Parthenium hysterophorous a poisonous and conceivable weed scatters quickly in waste and grazing land. In addition to allelopathic effect, number of human health problems like skin allergy, dermatitis and irritation to eyes is reported for this weed. Similarly it is indigestible and harmful to domestic animals and causes food shortage[11]. Considering its harmful effects it is selected to test phenol decontamination as a strategy to sort solution at two levels.

2. Experimental

2.1 Sample collection, preparation and characterization

Parthenium hysterophorous (PH) weed was collected from Margallah Hills Islamabad in the month of June (2013),

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weed was fresh and green at the time of sampling therefore to reduce water content it was sun-dried for about 5-6 days. The dried sample was crushed in a ball mill/grinder and passed through US standard sieve (mesh No. 80 mm) to obtain particle size of 180µm. Sieved samples were stored separately in polyethene bags to prevent readsorption of moisture before Phenol sorption. The surface functionality of samples was analyzed by FTIR spectrum (FTIR-8400, Shimadzu, Japan) in the wave number range of 4000-500cm^{-1}. The dried powder was ground with KBr (AR grade) at a ratio of roughly 1/1000. 500 mg of mass was made in to a pellet by pressing at 80KN for 1 min. After preparation, the pellet was analyzed immediately, and the spectra were recorded to 4cm^{-1} resolution. Surface morphology of biomass was observed by scanning electron microscopy ((SEM, JEOL model JSM-6490-A, Japan) at different magnifications.

2.2 Solutions and standardization

Reagents employed for batch biosorption study of Phenols are Chloroform, hydrochloric acid (conc.), potassium iodide (solid crystals), sulphuric acid (1N), standard sodium thiosulphate (0.025N), ammonium hydroxide (0.5N), starch (2g) dispersed in 100ml distilled water and methyl orange indicator (0.05ml dissolved in 100ml of distilled water). Bromate- bromide solution was prepared by dissolving anhydrous $KBrO_3$ (0.2784 g) in distilled water, to which 1g KBr crystals were added and diluted to 100mL. Phosphate buffer was prepared by dissolving potassium mono hydrogen phosphate (10.45 g) and potassium di-hydrogen phosphate (7.23 g) in 100mL of distilled water maintaining pH of solution at 6.8. Copper sulphate (100 g) and 4-Aminoantipyrine (2 g) was separately dissolved in 100 mL of distilled water. From 5% H_3PO_4 10 mL were diluted to 100mL in a volumetric flask. Potassium ferricyanide (2 g) was dissolved in 25ml of distilled water and stored in a brown bottle.

Phenol (1 g) was dissolved in 1000ml of freshly boiled, cooled distilled water and standardized. For standardization 50ml of stock phenol solution was added to100ml distilled water followed by 10ml of 0.1 N bromate-bromide solution and 1ml of concentrated HCl with gentle swirl.10 mL portions of bromate-bromide solution was added if brown colour of free bromine gives up then after 10 minutes KI (1g) was added swirled gently and kept for some time. A blank was prepared in the same manner using distilled water and 10ml 0.1 N bromate-bromide solution. Blank and sample were titrated with 0.025 N sodium thiosulphate using starch as an indicator. Concentration of phenol was calculated as:

$$\text{Mg/L Phenol} = 7.842\,[CA^{x}B - C] \qquad (1)$$

Where A, C stands for sodium thiosulphate (ml) used for blank and stock phenol solution respectively, and B for bromate-bromide solution (ml) used for stock phenol solution divided by 10.

2.3 Batch adsorption procedure

Standardize solution of phenol was employed after dilution for batch biosorption studies by using powder biomass of Parthenium hysterophorus. Sorption protocol was designed to investigate the effect of contact time and biomass dosage (0.01–0.06 g) on phenol remediation. Sorbate with fixed initial concentration was contacted with sorbent in separate flasks till attainment of equilibrium at room temperature. Contact of sorbate and sorbent was terminated by filtration according to predetermined time intervals. After filtration 0.5 mL of ammonium hydroxide, 0.2 mL of 4- Aminoantipyrene and 0.2 mL of Potassium ferricyanide solutions were added to 20ml of sorbate and blank by adjusting pH to 7.9 with phosphate buffer by using pH meter (inolab-720). Blank was used as reference for determining absorbance of phenol standard solution by UV/Vis spectrophotometer (PerkinElmer's LAMBDA 25). Phenol uptake by biomass was calculated as percentage (%R) using the equation:

$$\%R = \left(\frac{C_i - C_t}{C_i}\right)100 \qquad (2)$$

The biosorption efficiency q_e (mg/g) was calculated using:

$$q_e = \left(\frac{C_i - C_e}{W}\right)V \qquad (3)$$

where C_i, C_t and C_e (mg/L) are the liquid phase concentration of phenol initially, at time t and at equilibrium, respectively. V is the volume (L) of the solution and W is weight (g/L) of sorbent.

3. Results and discussion

3.1 Characterization of sorbent

3.1.1 FTIR analysis

Biomass in native and sorbed form was analysed using FTIR (Thermo Scientific USA NICOLET-6700) spectroscopy to figure out qualitatively basic functional groups on surface. FTIR spectrum of native PH reveals a less intense peak in the range 2915-2935cm^{-1} (**Figure 1**) corresponded to aliphatic C-H asymmetric stretching vibrations of methylene hydrogen's[12]. A peak at 2345–2364 cm^{-1} corresponded to P–H vibrations from phosphorus[13]. A sharp intense peak at 1739cm^{-1} corresponded to (C=O) stretching vibrations of aldehydes/ester[14] while peak at 1370cm^{-1} was attributed to weak C-O stretching vibrations in cellulose[15]. Prominent peaks between 1300 and 1000 cm^{-1} were due to the presence of phenolic and alcoholic moiety[16].

Appearance of strong broad band at 3600–3200 cm^{-1} corresponded to H-bonded OH groups of phenols[17] suggests phenol sorption from synthetic solution onto biomass surface. A band from 2923–2800 cm^{-1} on phenol adsorbed PH can be ascribed to aldehydes C-H group. Absorbance peak between 1600–1675 cm^{-1} could be attributed to C = C stretching vibrations of alkenes[16]. A band from 990–1050 cm^{-1} with a peak at 1016 cm^{-1} represented (P-O-C) stretching vibrations of aliphatic phosphates[12].

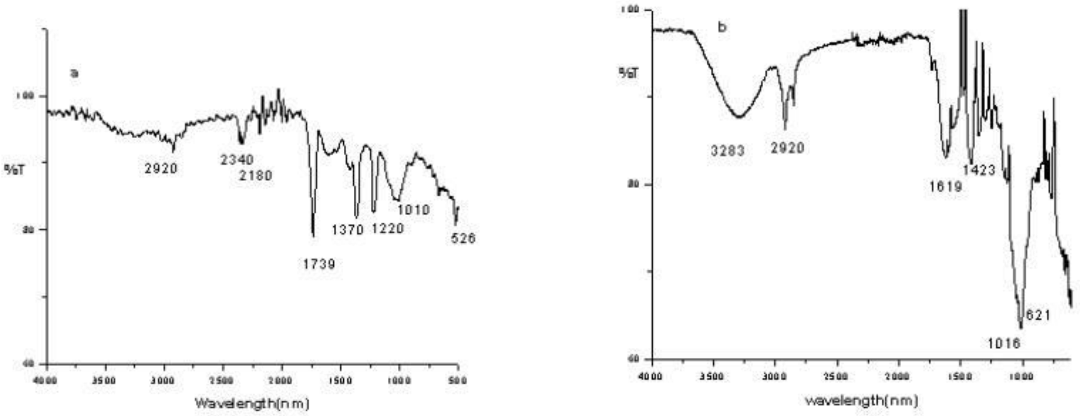
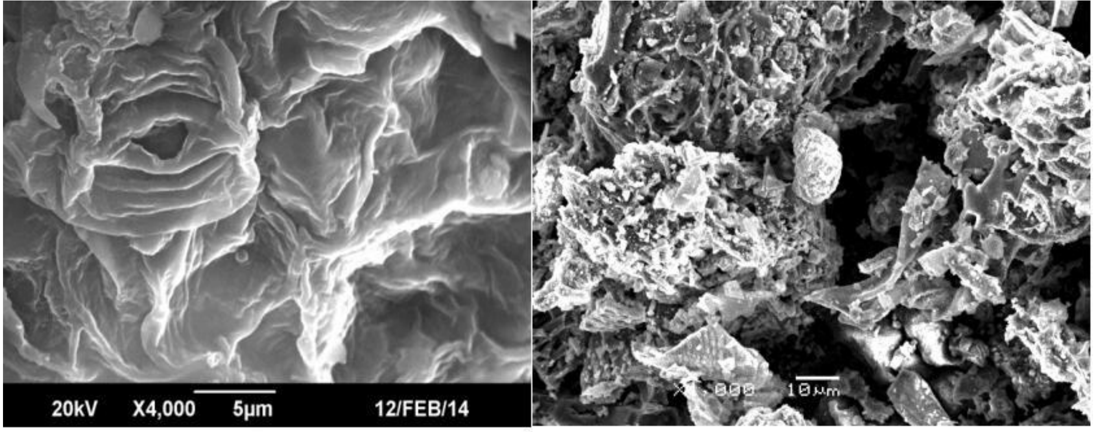


Figure 1. FTIR spectrum (a) of native and (b) phenol sorbed biomass

3.1.2 SEM analysis

The SEM images (**Figure 2A**) represent rough texture and heterogeneous distribution of pores on the surface of biomass. The pore openings apparent at 4000X magnification could offer accessibility of pollutant into internal pores[18] vital for the adsorption purposes[19]. Indication about biomass high surface area is reflected by **Figure 2B**, sort of swelling or scaling is apparent on biomass surface after loading of phenol.



(a) **(b)**

Figure 2. SEM images of native (**a**) and phenol sorbed (**b**) biomass

3.2 Time/dose optimization for adsorption

Concentration of phenol stock solution calculated by equation (1) comes out to be 17.432 mg/L; working standard of 4.5 mg/L concentration was prepared from it and contacted with 0.03 g of biomass in separate flasks to determine the influence of contact time. Absorbance of filtrate against blank was measured at 500 nm, revealing regular uptake of phenol establishing equilibrium attainment within 120 minutes (**Figure 3**)

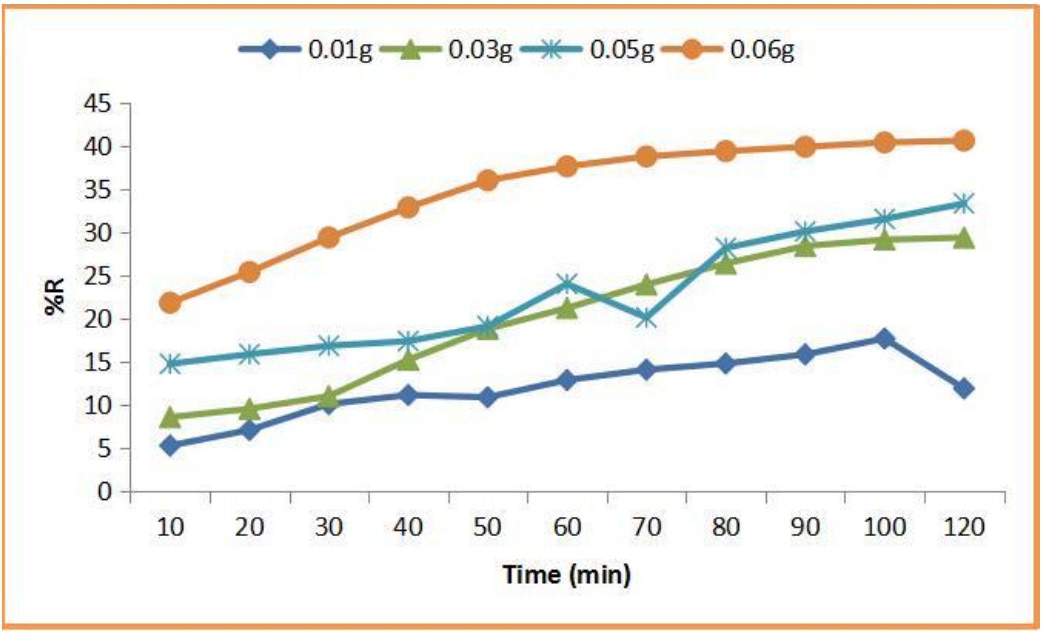


Figure 3. Effect of adsorbent dose on removal efficiency for phenol

The effect of dosage at values higher and lower than 0.03 g indicates that the removal efficiency generally increased as the dose concentration increased. Probably highest dose provided increased surface area or alternatively more sorption sites[20].

Similarly Zaid *et al*., (2008) reported K_d values increase with increasing dose, and removal enhancement from 25% to 90% by increasing adsorbent dose on the adsorption of MB dye[21].

3.3 Sorption kinetic study

To facilitate the mechanism of sorption reactions and to get valuable insight into the reaction pathways the study of kinetics in wastewater treatment is important. Therefore transport mechanism of phenol from aqueous media onto solid support is figured out through reaction and diffusion based models. The calculated and experimental values of sorption capacity (q_e), rate constants (k), and correlation coefficients (R^2) values are listed in **Table 1**.

3.3.1 Pseudo-first order

The linear form of Lagergren pseudo-first order kinetic model is:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \qquad (4)$$

Rate constant (k_1) and equilibrium amount of pollutant (q_e) can be obtained from slope and intercept of plot between log ($q_e - q_t$) against time (t).

	Pseudo first-order				**Pseudo second-order**			
m (g)	**q_e(exp) (mg/g)**	**q_e(cal) (mg/g)**	**K_1 (min^{-1})**	**R^2**	**q_e(cal) (mg/g)**	**h (mg/g min)**	**k_2 ($gmg^{-1}min^{-1}$)**	**R^2**
0.01	2.10	1.00	0.21	0.11	0.87	33.67	25.28	0.76
0.02	1.66	1.00	0.19	0.84	0.78	98.68	60.28	0.61
0.03	1.74	1.00	0.42	0.91	1.29	93.90	155.59	0.85
0.05	1.82	1.00	0.23	0.93	2.02	97.50	397.07	0.82
0.06	1.65	1.00	0.15	0.84	2.35	33.81	186.05	1.00

Table 1. Reaction based kinetics for phenol adsorption against adsorbent dosage

3.3.2 Pseudo-second order

Sorption capacity of the solid phase identification by linear form of pseudo-second order is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t \qquad (5)$$

Initial sorption rate, h (mg/g min), at t→0 can be defined as:

$$h = k_2 q_e^2 \qquad (6)$$

Linear plot of t/q_t against t result in a straight line, q_e and h values can be obtained from slope and intercept of plot (**Figure 4**). A decrease in the initial rate of adsorption was observed by increasing adsorbent amount, possibly due to the decrease in driving force (see **Table 1**). It is clear from values of h, that 0.02g is optimum mass at which maximum adsorption of phenol took place. Calculated biosorption capacity by pseudo-first order rate equation is found lower in comparison to experimental values. The correlation coefficients for both kinetic models is noted quite irregular and low, suggesting them as not rate limiting. Secondly the deduction of best fit for these models is inadequate owing to variations between actual and estimated values of q_e. Similarly less significance of pseudo first order kinetic model is reported for phenol sorption by activated carbon[22] and activated phosphate rock[23]. Whereas opposit to current study is favorability of pseudo second order model reported by elsewhere[24].

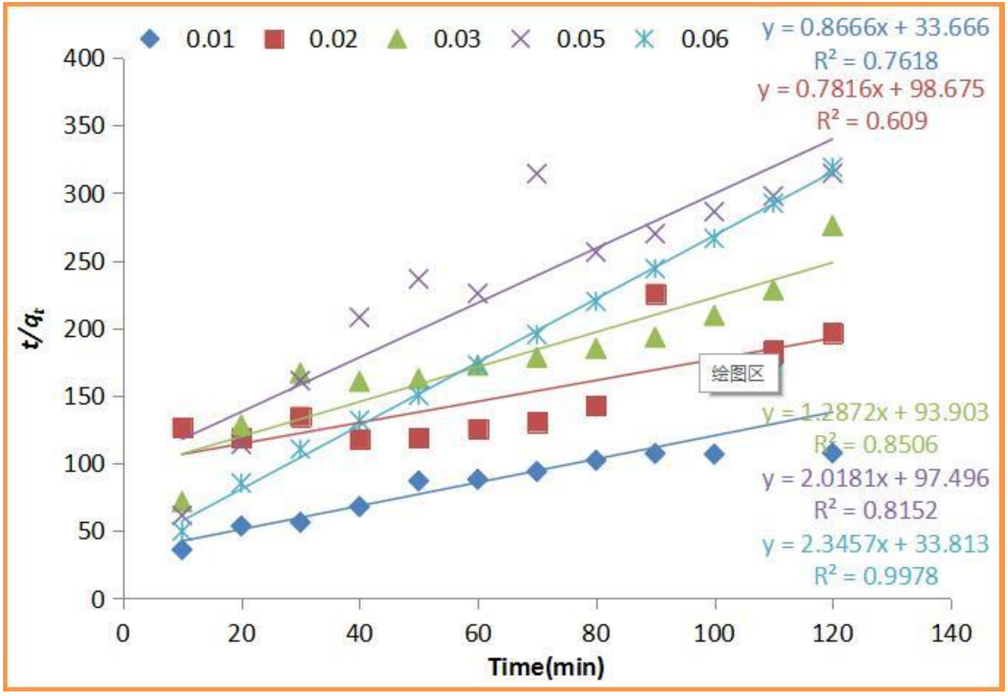


Figure 4. Pseudo second order kinetic plot for phenol sorption

3.3.3 Intraparticle diffusion model

The mechanism of diffusion was not identified by the kinetic models thus on the basis of theory projected by Weber and Morris (1962)[25], intrraparticle diffusion model (IPD) was used. It is an empirically found functional relationship which shows that variation of uptake is proportional to $t^{1/2}$ to a certain extent than with the contact time t. Equation can be represented as:

$$q_t = k_{id} t^{1/2} + C \qquad (7)$$

Where k_{id} is rate constant of intrraparticle (pore) diffusion (mg/g $\text{min}^{0.5}$) and C is boundary layer thickness. Straight line is obtained (**Figure 5**) by plotting graph between q_t and $t^{1/2}$. The values of k_{id} indicate that the intrraparticle diffusion becomes more prominent with an increase in adsorbent amount (see **Table 2**). Similarly values of intercept C also increase and by expansion, it indicates that boundary layer effect increases at alleviating dosage.

3.3.4 The Elovich model

The linear form of Elovich equation is:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \qquad (8)$$

Where q_t is the amount adsorbed (mg/g) at time t, α is the initial sorption rate, (mg/g min), and β is the desorption constant (g/mg). Plot of q_t versus lnt give straight line and the values of α and β were calculated from slope and intercept of straight line. It can be figured out (**Table 2**) from values of α that adsorption rate decreases by increasing adsorbent amount, simultaneously desorption of sorbed phenol molecules from PH surface is indicated by increasing trend of β values

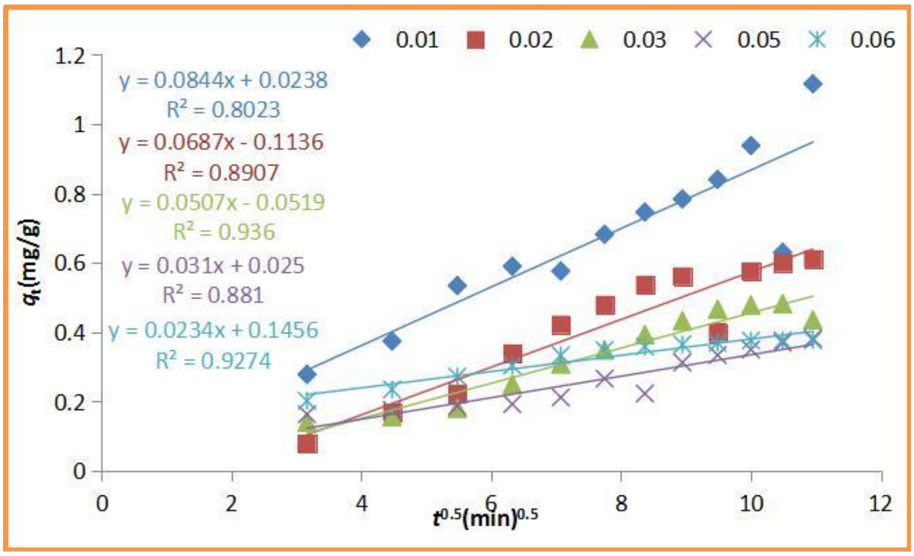


Figure 5. Intraparticle diffusion model for the sorption of phenol

Correlation coefficient values signify supremacy of IPD model to Elovich, which reveals that the molecular diffusion of phenol molecules on the surface of adsorbent played a major function in its removal. Similarly IPD significance for phenol adsorption is reported by Ruey *et al*., (2000) on activated carbon Prepared from Plum Kernels and Abdel-wahab *et al*., (2013) on Luffa cylindrica fiber[26,27].

m **(g)**	**Intra particle diffusion**			**Elovich**		
	k_{ip} (mg/g/min$^{0.5}$)	**C**	**R^2**	**α** **(mg/g/min)**	**β** **(g/mg)**	**R^2**
0.01	0.08	0.02	0.80	0.36	3.34	0.46
0.02	0.07	-0.11	0.89	0.27	3.59	0.66
0.03	0.05	-0.05	0.94	0.21	4.81	0.71
0.05	0.03	0.03	0.88	0.12	8.68	0.55
0.06	0.02	0.15	0.93	0.11	10.91	0.64

Table 2. Estimated rate constants for phenol adsorption by diffusion based model

3.4 Sorption isotherms study

Adsorption isotherms are used to describe the interaction of solute particles with adsorbents, and are significant for optimizing the use of adsorbents[28]. Most frequently experienced isotherms are Langmuir and Freundlich. Recent study explores Temkin, Dubinin-Radushkevich and Flory-Huggins isotherms including most tested one for sorption of phenol by variable doses of adsorbent.

3.4.1 The Langmuir isotherm

Langmuir model assumes monolayer adsorption of material in liquid over a homogenous surface of adsorbent at a constant temperature; its equation in linear form is:

$$\frac{C_e}{q_e} = \frac{1}{q_m \mathrm{K_L}} + \frac{C_e}{q_m} \qquad (9)$$

where q_m is the maximum adsorption capacity (mg/g) and K_L is a constant associated to the binding sites affinity (L/mg). A graph of C_e/q_e versus C_e yields a straight line with a slope and intercept from which q_m and k_L can be calculated. Value of q_m was found contradictory to the experimentally determined biosorption capacity, secondly value of R^2 (0.28) shows that Langmuir model is not followed for adsorption of phenol by PH.

3.4.2 Freundlich Isotherm

Freundlich isotherm model reported in literature[29,30], assumes that the process of adsorption takes place on a non-uniform surface. The linear form of equation is:

$$log q_e = log \mathrm{K_F} + \log C_e^{1/n} \qquad (10)$$

Where K_F ((L/mg) is used to express the adsorption capacity and 1/n is the strength of adsorption, it indicates both the heterogeneity of the adsorbent sites as well as relative distribution of energy. Nature of sorption identified from value of 1/n (0.29) indicates its favourability, as type of isotherm will be irreversible if (1/n = 0), favourable (0 < 1/n < 1), and unfavourable (1/n > 1) (Theivarasu and Mylsamy, 2011). Still R^2 does not support Freundlich model as best fit.

3.4.3 Temkin Isotherm

This model assumes that the adsorption process is indirectly affected by the adsorbate/adsorbent interactions (Dada, 2012). Expressed in linear form as:

$$q_e = \frac{\mathrm{RT}}{b_T} ln\mathrm{K_T} + \frac{\mathrm{RT}}{b_T} lnC_e \quad (11)$$

where R is general gas constant (0.008314 kJ/mol K), T is absolute temperature (K), $1/b_T$ is sorption heat constant (KJ/mol), and K_T (L/g) is adsorption capacity referred as adsorption

Isotherms	parameters	Values	Isotherms	Parameters	Values
Langmuir	q_m (mg/g)	-0.28	Dubbin-Radushkevich	K_{DR}	10.97
	K_L(L/mg)	-0.36		q_m	4.81
	R^2	0.31		R^2	0.53
Freundlich	N	0.29		E	0.21
	K_F(mg/g)	0.72	Flory Huggins	α_{FH}	-2.87
	R^2	0.57		K_{FH}	0.06
Temkin	B	0.98		R^2	0.90
	K_T	-2.87		ΔG^o	-7.09
	R^2	0.67			

Table 3. Isotherms model constants and their respective coefficients for phenol sorption constant. Values of $1/b_T$ and K_T can be calculated from slope and intercept of a plot between q_e and lnC_e. Heat of sorption identified by this model indicates weak sorbent sorbate interaction.

3.4.4 The Dubinin-Radushkevich isotherm

This isotherm is reported by Radushkevich (1949) and Dubinin (1965) describing a relation between sorption curve and the porous structure of the sorbent[31]. It is generally represented by equation:

$$\ln q_e = \ln q_m - \mathrm{K_{DR}} \varepsilon^2 \qquad (12)$$

where K_{DR} is a constant and is associated with the mean free energy of sorption per mole of the sorbate. This energy can be calculated by equation,

$$E = \frac{1}{\sqrt{2\mathrm{K_{DR}}}} \quad (13)$$

The calculated value of E is 0.21 KJ/mol less than 8 KJ/mol[32], indicates physiosorption of phenol on PH surface. The calculated maximum biosorption capacity was noted very high than experimental value in addition to low value of correlation coefficient.

3.4.5 Flory Huggins isotherm

The degree of surface coverage of adsorbate on adsorbent can be expressed in linear form according to Flory – Huggins model as:

$$\log\left(\frac{\theta}{C_e}\right) = \log\mathrm{K_{FH}} + \alpha_{FH}\log(1-\theta) \qquad (14)$$

where θ is the degree of surface coverage, can be computed by:

$$\theta = \frac{1-C_e}{C_i} \qquad (15)$$

α_{FH} is the number of metal ions occupying sorption sites and K_{FH} the equilibrium constant of adsorption[33]. The values of K_{FH} and α_{FH} can be obtained from intercept and slope of the plot of log (θ / C_e) versus log $(1-\theta)$ respectively. Moreover the equilibrium constant K_{FH} can be used to compute the Gibbs free energy for sorption process. The Gibbs free energy is related to equilibrium constant as follow:

$$\Delta G^{\circ} = -\mathrm{R}T\ln\mathrm{K_{FH}} \qquad (16)$$

A positive correlation is inferred from data of surface coverage (θ) with increase in sorbent concentration, the effect is found increasing from 21% to 41% by increasing biomass dosage from 0.01g to 0.06g. The negative value of ΔG^o shows feasibility and spontaneous nature of the process. Fitness approximation calculates phenol sorption onto PH by this model due to highest R^2 value (see **Table 2**).

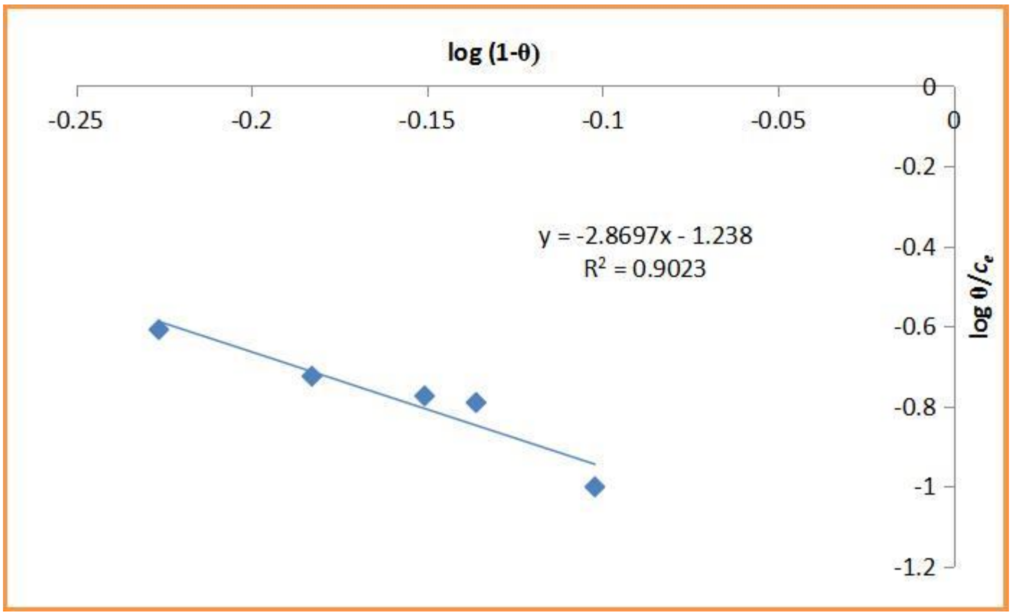


Figure 6. Flory Huggins model for adsorption of phenols

Similarly Flory Huggins isotherm was appreciably followed for the adsorption of Cu(ii) on coconut (Cocos nucifera L.) coir dust and for adsorption of lead (ii) ions from aqueous solution using coir dust (cocos nucifera l.) And it's modified extract resins[34]. On the contrary Langmuir and Freundlich isotherm models were followed for the adsorption of phenol on granular activated carbon from nutrient medium[35], and Cr-bentonite[36].

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Conclusions

The positive correlation was noted for adsorption of phenol enhancement with an increase of biomass dosage. The Intraparticle diffusion of phenol onto adsorbent surface was identified to be the rate limiting step. Flory-Huggins gave a better fit to all adsorption isotherms than the Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich, and the remediation process was figured out as a physical adsorption rather than a chemical one.

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