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Liquid-phase adsorption of phenol onto blended adsorbents through bioremediation

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ABSTRACT

The present studies aimed toward evaluating the feasibility of using the soil-agro blend as potential low-cost adsorbents for the removal of phenol from its aqueous solution. Thus, batch mode experiments were carried out for optimization of the adsorption parameters such as adsorbent dosage, contact time, and equilibrium time for varying initial phenol concentrations. A comparison of different isotherm models varying from two to five parameters as well as several kinetic models was applied to the experimental data. Results show that the higher order models were found to agree well with the experimental data. The desorption studies of phenol from adsorbed adsorbent carried and the optimized duration of desorption of adsorbate as 160 min (with alkali-leaching pretreatment). For complete removal of phenol from the desorbed adsorbent, biodegradation using cow dung was carried. The results show that phenol from 35 mg/L to below the detected limits within a period of 10 h.

Keywords: Adsorption; Isotherm models; Desorption; Biodegradation

1. Introduction

The major source of phenolic compounds is industrial wastewaters such as oil refineries, gasoline, coal, paper, leather, paints, textile, rubber, steel, and pharmaceutical industries. At low concentrations, these compounds are toxic and before discharging the wastewater to the environment prior treatment is necessary. The most commonly adopted method is recovering phenol from wastewaters; the best method is destructing the waste by microbial degradation, adsorption, chemical oxidation, and reverse osmosis are being used for removing phenols from wastewater. Adsorption is an effective separation process for treating industrial and domestic effluents. Activated carbon (AC), one of the most commonly used adsorbents all over the globe, because of high internal surface area/pore structure. AC can be manufactured from a number of raw materials including wood, coconut shell, and coal having a potential for adsorption of molecules from both the liquid and the gas phases. Over the last century, extensive researches have been carried out to the study of adsorption for the removal of aqueous organic materials, such as phenols and phenol derivatives using AC [1,2]. Although such approach is certainly cost-effective (compared with other separation methods) and ease in operation, yet there are certain specific disadvantages, namely, limitation in natural resources, prohibiting initial cost of the adsorbent, the increasing problem of disposal of adsorbed adsorbent (and/or expensive regeneration). The adsorption process is one of the most important wastewater treatment process chiefly deals with AC. Many researchers are understood and identify cost-effectiveness of AC, they have studied the practicability of using cheap, locally available materials as potential adsorbents. There has been a growing need for a development of low-cost substitute adsorbents [3], involving both chemical as well as thermal regeneration methods. However, due to high expense involved in these procedures as well as the production of additional effluents leading to further loss of the adsorbent necessitates search for low-cost adsorbents (i.e., available free of cost or low-cost as compared with ACs). An ample diversity of materials has been investigated [4] for this purpose and they can be classified into three categories: (1) natural materials, (2) agricultural residue, and (3) industrial wastes.

Since last decade, utilization of natural soil/clay minerals as low-cost adsorbents (such as montmorillonite, kaolinite, and illite) has been increasing interest for removal of organic and toxic metals from the industrial wastewaters, because of the profusion of soil/clay in most continents of the world [5–9]. The application of sorption technique removal of phenol using soil/clay has been tested [10]. In addition, mixed sorbent systems, such as the sorption of lead III on china clay and wollastonite [11], heterogeneous mixture of alumina and clay to remove the color of dye [12], and the mixture of clay–wood sawdust [13], have also been investigated.

The present works focus on evaluating the adsorption capacity, using the mixture of natural soils (locally available soils, i.e., two major clay types of southern India), and agro residues, without any adaptation, to assess their virgin adsorption potentials. Accordingly, the objective of the present study is to evaluate the usefulness of abovementioned soil-agro blends for adsorption of phenol from aqueous solution.

2. Materials and methodology

The concentration of phenol was determined by spectrophotometric analysis using 4-aminoantipyrine method (at a wavelength of 500 nm) [14]. The equilibrium concentrations were determined using an UV/Vis spectrophotometer (characteristic peak at 270 nm).

Black gram (*Cicer arietinum*) and green gram (*Vigna radiat*a) are important pulse crops in India. During milling of gram into dhal about 25% is a by-product. Currently, it is used as cattle feed or waste and, therefore, it does not have any commercial value [15]. Rice husk (RH), is a by-product of the rice milling industry and huge amount of residue about 20% whole rice produced on weight basis [16]. The black gram husk (BGH), green gram husk (GGH), and RH were washed with water to remove dirt and other particulate matter. Washing and boiling were followed repeatedly by using distilled water to remove color. The washed and boiled BGH, GGH, and RH were oven dried at 105°C for 24 h crushed and stored in desiccator for further studies.

In this work, soil-agro residue blend (w/w) was used to improve the adsorption capacity of the adsorbent. The adsorption capacity has been increased by blending soil with agro residue. The presence of organic matter–clay complexes in most of the soils needs to be considered in evaluating the importance of organic matter in phenol adsorption. However, at higher organic matter (≤50%), adsorption will occur mostly on organic surfaces. This is due to the agro residue (organic matter) coat the clay present in the soil. This was supported by Stevenson [17] quoted Walker and Crawford indicated that up to an organic matter of about 10%, both mineral and organic surfaces are involved in adsorption. Stevenson pointed out that the amount of organic matter required to coat the clay will depend on the soil type and the kind and amount of clay that is present. As studies reveal various blends proportions were studies for adsorption of phenol and the optimum dosage of blend was found at 25% of organic matter.

2.1. Adsorption studies (batch studies)

The adsorption batch experiments were carried at room temperature (30°C ± 2°C). For each experiment, a known concentration of 100 mL of phenol, at varying dosages of adsorbents were taken in conical flasks (250 mL) and sample was kept in a shaking Water Bath Temperature controller of 220 rpm at 30°C ± 2°C were equilibrated for 24 h and equilibrium phenol concentration was estimated, by measuring absorbance using double beam UV–Vis spectrophotometer (Model no. SL-164; Elico, India) at 270 nm. The amount of adsorption at equilibrium, q_e (mg/g) and the percentage adsorption (%) was computed as follows:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

$$\text{Percentage adsorption} = \frac{C_0 - C}{C_0} \times 100 \tag{2}$$

where C_0 is the initial sorbate concentration (mg/L), C_e is the equilibrium concentration in the solution (mg/L), V is the solution volume (L) and 'm' is the mass of adsorbent (g).

2.2. Theory of adsorption equilibrium

In this study, array of different isotherms have been proposed, these isotherms were derived based on the theoretical foundation and some being of a more empirical nature. A numerous of these isotherms are valid over small relative pressure ranges but do not fit the experimental data when tested over the full range of relative pressures. A huge number of researchers working in the field of wastewater treatment for the design of AC – polluted systems have been determined by Langmuir and Freundlich isotherm equations. In this work for removal of phenol, the adsorption potential of the soil and soil-agro-based adsorbents have been studied using adsorption isotherms and tested against multiparameter model (up to five parameters) Langmuir, Freundlich, modified Langmuir-1, modified Langmuir-2, Dubinin–Radushkevich, and Temkin (two-parameter models), Langmuir–Freundlich, Redlich–Peterson, Sip, Fritz–Schlunder model, Radke–Prausnitz model, Toth model, and Jossens model (three-parameter models), Fritz–Schlunder model, Baudu (four-parameter models), Fritz–Schlunder (five-parameter model) isotherm models.

The phenol adsorption capacity of soil-agro residue was used in this study and the pH of the adsorbent and adsorbate mixture ranged between 4 and 6, because of the exchangeable cations in the soil-agro residue blend. The equilibrium mixture was adjusted to pH 6.0 and further batch studies were carried out at 6 h equilibrium time at room temperature of 30°C ± 2°C. The surface functional groups play key roles in the adsorption mechanism. Therefore, spectroscopic studies (Fourier transform infrared spectroscopy [FTIR]) were conducted.

The optimization studies were carried out by adding different dosages of adsorbents per unit mass of adsorbate still the equilibrium was attained. A variety of kinetic models (namely, pseudo-first-order, pseudo-second-order, and the Elovich and intra-particle diffusion) were used to study the kinetics of adsorption by four soil-agro residue blends.

To study the applicability of different isotherm models, a normalized standard deviation was used to compare the experimental data with predicted data. The equation is as follows:

$$\Delta q = 100 \times \sqrt{\frac{\sum\left[\left(q_{\exp} - q_{\text{pre}}\right)/q_{\exp}\right]^2}{N-1}} \tag{3}$$

where N is the number of experimental data points, $q_{\exp}$ and q_{pre} (mg/g) are the experimental and the predicted values of the equilibrium adsorbate solid concentration in the solid phase, respectively.

The phenol adsorption on to the six soil-agro residue blends isotherm shown in Fig. 1. Phenol could be adsorbed by the soil-agro residue either in the neutral form or in the negatively charged form [18]. Due surface charges in soil-agro residue blends (includes both inorganic and organic components) indicate the high capacity for phenolic acids. The silicate clay minerals contributes ionic charges on the inorganic compounds (which carry a permanent charge) and non-crystalline materials are indispensably attributable to the great bonding of their positively charged Al–OH and Fe–OH functional groups toward and also the charges by the organic compounds (halogenated organic compounds), the negatively charged carboxyl and phenolic hydroxyl groups [10,18].

2.3. Kinetic studies

The cost and performance of a product are always of concern to control process efficiency. Therefore, the sorption capacity and required contact time are two of the most important parameters to understand. Sorption equilibrium is established when the concentration of sorbate in the bulk solution is in dynamic balance with that of the interface. An equilibrium analysis is the most important fundamental information required to evaluate the affinity or capacity of a sorbent. However, thermodynamic data can predict only the final state of a system from an initial non-equilibrium mode. It is therefore important to determine how sorption rates depend on the concentrations of sorbate in solution and how rates are affected by sorption capacity or by the character of the sorbent. From the kinetic analysis, the solute uptake rate, which determines the residence time required for completion of the sorption reaction, may be established. Various kinetic models have been used by researchers, using the pseudo-first-order [19,20] and pseudo-second-order models [21].

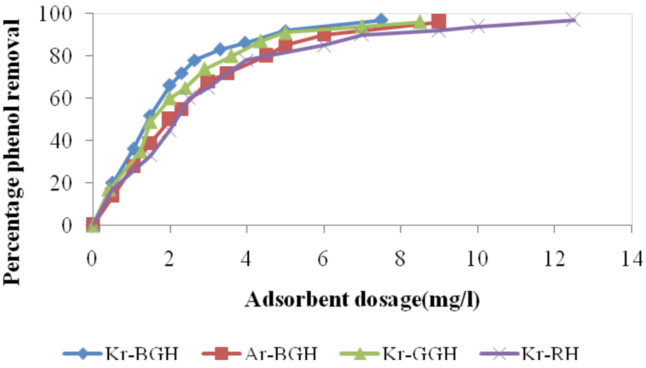

Fig. 1. Effect of blend dosage on the removal of phenol.

2.3.1. Pseudo-first-order model

The Lagergren model of pseudo-first-order kinetic rate equation is described by the following equation:

$$\frac{dq_t}{dt} = k_t(q_e - q_t) \tag{4}$$

where k_t is the rate constant. By integrating the above equation with initial conditions of $q_t = 0$ at $t = 0$ and at $t = t$, $q_t = q_t$, Eq. (4) becomes:

$$\log(q_e - q_t) = \log q_e - \frac{k_t}{2.303}t \tag{5}$$

where q_e is the adsorption at equilibrium in mg/g. Slope of k_t was calculated by plotting $\log(q_e - q_t)$ vs. t for different concentrations of phenol. The results of k_t and correlation coefficients were shown in Table 1.

2.3.2. Pseudo-second-order kinetic model

Aharoni and Tompkins [22] proposed the pseudo-second-order kinetic model as given below:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{6}$$

where k_2 is the second-order rate constant (g/mg min). The values of k_2 and q_e were calculated by plotting a graph between t/q vs. t. The results of k_2 and correlation coefficients are shown in Table 1. It can infer from the table that the second-order kinetic model is better than the first-order kinetic model.

2.3.3. The Elovich kinetic equation

The Elovich is one of the constructive kinetic models as follows [21]:

$$\frac{dq_t}{dt} = \alpha\exp(x\beta q_t) \tag{7}$$

where α is the initial adsorption rate (mg/g min) and β is the desorption constant (g/mg).

To simplify the Elovich equation, assumed $\alpha\beta t >> t$ and by applying boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, Eq. (7) becomes:

$$q_t = \left(\frac{1}{\beta}\right)\ln(t + t_0) - \left(\frac{1}{\beta}\right)\ln t_0 \tag{8}$$

where $t_0 = 1/(\alpha\beta)$. If t is much larger than t_0, Eq. (8) can be simplified as:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \tag{9}$$

The term 1/β indicates the number of sites available for adsorption. The values of α, β and correlation coefficients were shown in Table 1.

Table 1
The adsorption kinetic rate model constants for the Kr-GGH, Kr-BGH, Ar-BGH and Kr-RH (temperature 30°C ± 2°C at pH ~6)

Adsorbent	Initial concentration, C_0 (mg/L)	Experimental, Q_e (mg/g)	Pseudo-first-order			Pseudo-second-order				Elovich		
			k_1	r^2	Calculated, Q_e (mg/g)	k_2	h	r^2	Calculated, Q_e (mg/g)	β	α	r^2
Ar-BGH	20	2.5	0.0069	0.985	2.0893	0.0051	0.0416	0.988	2.8653	1.7422	0.1041	0.982
	40	5.6667	0.0046	0.991	4.9204	0.0014	0.0631	0.965	6.8027	0.7123	0.1477	0.951
	60	8.3333	0.0092	0.991	6.7143	0.0020	0.1817	0.996	9.434	0.5495	0.4887	0.992
	80	12.000	0.0069	0.993	11.4551	0.0004	0.106	0.981	17.2414	0.2781	0.2516	0.992
	100	16.000	0.0092	0.996	14.1254	0.0008	0.2803	0.997	18.8679	0.2504	0.6269	0.993
Kr-BGH	20	2.53333	0.0092	0.994	2.9444	0.0042	0.039	0.997	3.0395	1.5244	0.0855	0.996
	40	4.93333	0.0115	0.997	6.6222	0.0022	0.0816	0.996	6.0606	0.7337	0.1674	0.982
	60	7.33333	0.0046	0.995	9.3972	0.001	0.0783	0.989	8.8496	0.5277	0.1752	0.980
	80	10.2667	0.0069	0.996	9.1622	0.0008	0.1327	0.992	12.987	0.3554	0.2885	0.980
	100	12.6667	0.0092	0.994	11.1429	0.0007	0.1754	0.997	16.129	0.2803	0.3701	0.990
Kr-GGH	20	3.5235	0.0069	0.985	2.9444	0.0036	0.0586	0.988	4.0486	1.2361	0.1468	0.982
	40	7.9333	0.0046	0.983	6.6222	0.0036	0.0586	0.971	4.0486	0.5244	0.232	0.956
	60	11.6667	0.0092	0.991	9.3972	0.0015	0.2543	0.996	13.1579	0.3925	0.684	0.992
	80	16.800	0.0069	0.993	9.1622	0.0002	0.1484	0.981	24.3902	0.1986	0.3524	0.992
	100	22.6333	0.0092	0.995	11.1429	0.0005	0.3883	0.997	27.027	0.1777	0.8723	0.993

2.3.4. Intra-particle diffusion model

Weber and Morris [23] proposed intra-particle diffusion model to investigate the rate-limiting step, the model is as follows:

$$k_t = \frac{q_t}{t^{0.5}} \tag{10}$$

where q_t refers to the amount of phenol adsorbed in mg/g at time t.

2.4. Adsorption isotherms

In order to establish appropriate correlation for the equilibrium curves, it is most important to optimize the design parameters of adsorption system. In this study, a range of isotherm models varying from two parameters to five parameters mention are being used to describe the equilibrium nature of adsorption.

Langmuir's equation is the most commonly used two-parameter equations and the equation expressed as follows:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \tag{11}$$

where q_e is the amount of phenol adsorbed per unit weight of adsorbent at equilibrium (mg/g), C_e is the equilibrium concentration of the phenol in the bulk solution (mg/L), q_m is the maximum adsorption capacity (mg/g) and b is the constant related to the free energy of adsorption (L/mg).

The Freundlich isotherm equation is the most commonly used isotherm. The equation was derived based on heterogeneous adsorptive energies on the adsorbent surface and the equation expressed as follows:

$$q_e = k_f C_e^{1/n} \tag{12}$$

where k_f is a constant, it indicates the relative adsorption capacity of the adsorbent ($(\mathrm{mg}^{1-(1/n)}\ \mathrm{L}^{1/n})/\mathrm{g}$) and n is a constant, intensity of adsorption.

The Redlich–Peterson equation is expressed as follows:

$$q_e = \frac{K_{\mathrm{RP}} C_e}{1 + \alpha_{\mathrm{RP}} C_e^{\beta}} \tag{13}$$

where K_{RP} (L/g) and α_{RP} $(\mathrm{L/mg})^{\beta}$ are Redlich–Peterson isotherm constants and β is the exponent which lies between 1 and 0.

3. Results and discussion

3.1. Effect of adsorbent dosage

To investigate the adsorption capacity of blends of agro residue with soils and posses the system of soil organic complex. Since, agro residues contain mainly complex carbon compounds originating from cell walls (cellulose, hemicelluloses, etc.), the rate of decomposition varies from fast to slow (cellulose, fats, waxes, and resins) to very slow (lignin). Fig. 1 shows the amount of phenol removed as a function of adsorbent dosage from the solution. For the blends, adsorbent dosage was varied from 50 to 1,200 mg and equilibrated for 24 h. As evident from Fig. 1, to remove 96% of phenol, the optimum blend adsorbent dosage required were found to be 7.5, 9.0, 8.5l, and 12.5 g/L for Kr-BGH, Ar-BGH, Kr-GGH, and Ar-RH, respectively. Thus, these soil-agro residue based adsorbents follow the trend as Kr-BGH > Kr-GGH > Ar-BGH and Ar-RH.

3.2. Effect of contact time on adsorption by four soil-agro residue blends

The study results disclose that the uptake of adsorbate is fast (in first hour of adsorption, it varies from 38% to 64%) at the initial stages of the batch studies, and thereafter, it becomes slower near the equilibrium (within the next 5 h the removal of phenol varies from 40% to 25%). Fig. 2 shows that the rate of phenol removal is found to be surface sites are available for adsorption during the initial stage, and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases. Aqueous phenol solutions with different initial concentrations (C_0) were kept in contact with the adsorbents for 24 h. It was observed that the equilibrium adsorption of the phenol, which was observed at 24 h, was more or less achieved at 6 h itself (with respect to the residual concentrations) and hence 6 h was used as equilibrium time for adsorption in case of all the six adsorbents.

3.3. Kinetic results interpretation

Finding the rate-limiting step is the one of the most important prediction in the adsorption process prediction and also helps for design of economical wastewater treatment process. The mechanism involved in the solid–liquid phase adsorption can be either boundary layer diffusion (external mass transfer) for non-porous media or intra-particle diffusion for porous media [24]. The results of correlation coefficients for pseudo-first-order and pseudo-second-order models are shown in Table 1. But, for pseudo-first-order, Q_{cal} and Q_{exp} values showed striking differences. Therefore, from the results it was found to favor pseudo-second-order reaction and the pseudo-second-order kinetic model was found to be the rate-limiting step.

To explain the present adsorption phenomena the Elovich kinetic model was used for all sorbate–sorbent system. A graph between q_t vs. $\ln(t)$ was drawn, which shows good linearity (r^2 values varies from 0.951 to 0.996), and has been interpreted to understand the initial rate of the process

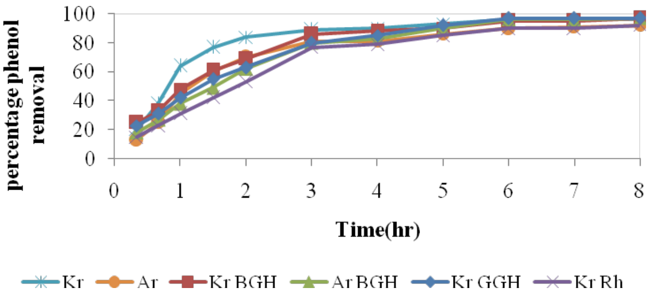

Fig. 2. Effect of soil and blend dosage on the removal of phenol.

as well as the nature of sites involved in the adsorption process. The mechanism can be explained by the following assumptions, the first explanation postulates during chemosorption the release of energies is proportioning to the extent of coverage and the second explanation assumes the heterogeneity in the nature of the active sites involves the variation in activation energies required for chemisorption [25]. Based on the values of α and β are applied in Eq. (10) at all concentrations for soil-agro residue blends, $t >> t_0$ (with 't_0' values varying between 14.29 and 3.72 min), thereby justifying the first assumption of the occurrence of chemisorptions. Second, with increasing the initial phenol concentration (from 20 to 100 mg/L), the β values showed a general trend of reduction (from 1.53 to 0.28 g/mg for Kr-BGH, from 1.74 to 0.25 g/mg for Ar-BGH, from 4.34 to 0.258 g/mg for Kr-RH and from 1.24 to 0.178 g/mg for Kr-GGH). Thus, $1/\beta$ showed a distinct increase in both the soils as well as soil-agro residue blends with an increase in concentration, again reinforcing the occurrence of chemisorption's in both the soils as well as for the soil-agro blend adsorbate systems.

3.4. Adsorption non-linear isotherm analysis

This phase of the study involved evaluating the adsorptive capacity of each candidate adsorbent for phenol. Adsorption isotherms were generated and the adsorptive capacity interpreted using the different non-linear isotherm models, ranging from two- to four-parameter isotherm models. To select the best isotherm model correlation coefficient and the average percentage errors (APEs) were calculated to select the best isotherm model. To calculate the APEs the following equation is used:

$$\text{APE} = \frac{\sum_{i=1}^{N} \left| (q_e)_{\text{experimental}} - (q_e)_{\text{calculated}} \right| / (q_e)_{\text{experimental}}}{N} \times 100 \qquad (14)$$

3.5. Bi-parameter model

Modified Langmuir-1, modified Langmuir-2, Temkin, and Dubinin–Radushkevich have modified the original second-degree isotherm models (namely, Langmuir and Freundlich). Model fits for the two-parameter isotherms along with experimental data were presented in Figs. 3–6 for soil-agro blend adsorbents. Tables 2 and 3 show the values of model constants along with corresponding correlation coefficient, APE for all sorbent–sorbate system.

The Langmuir isotherm model represents the monolayer coverage for the soil-agro blends. The sorption capacity, q_m, which is a measure of the maximum sorption capacity corresponding to complete monolayer coverage showed that the soil-agro blends based adsorbents seemed to have high monolayer adsorption capacities than soil adsorbent system, except for Ar-RH adsorbent system. The sorption capacities of the different sorbent–sorbate system are Kr-BGH soil-agro blend (65.87 mg/g), Kr-GGH soil-agro blend (56.95 mg/g), Ar-BGH soil-agro blend (44 mg/g), and Ar-RH soil-agro blend (37.81 mg/g). After addition of agro residue to the soil sorbent–sorbate system the adsorption capacities were improved.

The adsorption coefficient, b, related to the apparent energy (surface energy) of sorption, for Kr-BGH (0.1654 L/g),

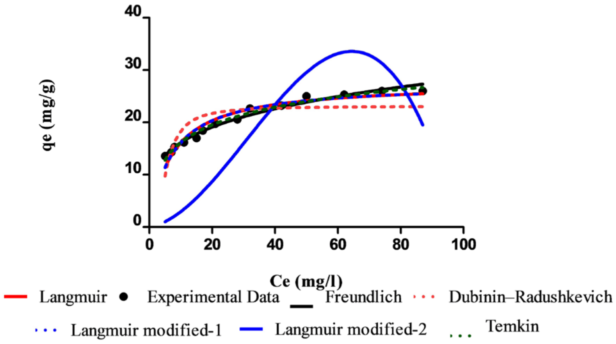

Fig. 3. Two-parameter isotherm models for Kr-BGH.

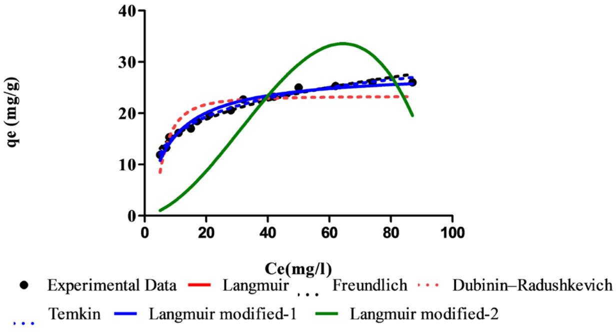

Fig. 4. Two-parameter isotherm models for Ar-BGH.

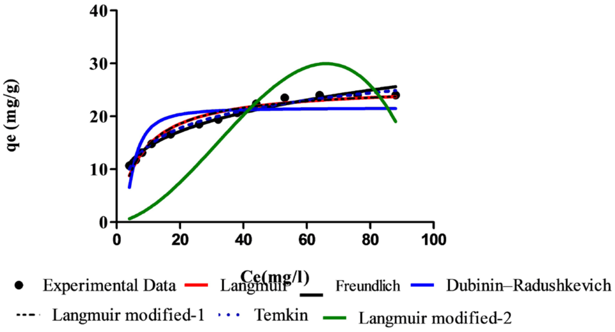

Fig. 5. Two-parameter isotherm models for Kr-GGH.

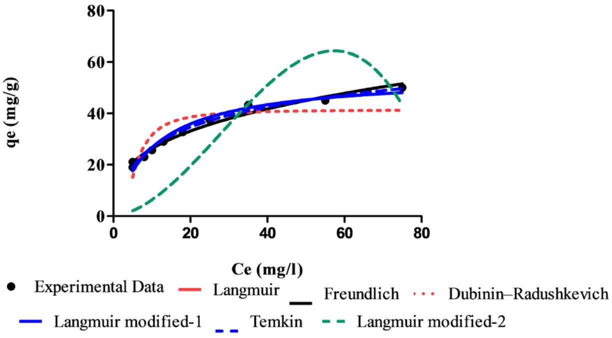

Fig. 6. Two-parameter isotherm models for Ar-RH.

Table 2
Details of two-parameter isotherm constants for soil and soil-agro blend

Type of isotherm \ type of adsorbent	Kr-BGH	Ar-BGH	Kr-GGH	Ar-RH
Langmuir				
b (L/mg)	0.1654	0.115	0.05854	0.08647
q_m (mg/g)	65.87	48.2	56.95	37.81
r^2	0.9914	0.9868	0.9935	0.9953
Freundlich				
k_f	22.62	12.87	8.739	7.861
n	4.153	3.729	2.509	2.907
r^2	0.9446	0.9684	0.9633	0.9561
Modified Langmuir-1				
B	0.1654	0.07694	0.05854	0.08647
n	–0.7329	–0.6861	–0.7075	–0.6358
r^2	0.9914	0.9884	0.9935	0.9953
Dubinin–Radushkevich				
K_{dr}	56.32	40.89	42.73	29.73
B	2.302	13.73	14.07	6.854
r^2	0.8151	0.9356	0.862	0.8397
Temkin				
B	0.2158	0.2401	0.2079	0.3163
A	3.012	0.8722	0.6245	0.9216
r^2	0.9845	0.9678	0.9832	0.9949

Table 3
Isotherm parameters (two parameters) APE and correlation coefficients

Adsorbent	Kr-BGH		Ar-BGH		Ar-RH		Kr-GGH	
Isotherm	APE	r^2	APE	r^2	APE	r^2	APE	r^2
Langmuir	2.370	0.991	1.669	0.988	1.683	0.995	3.706	0.994
Freundlich	5.795	0.945	3.475	0.934	8.765	0.956	7.945	0.963
Modified Langmuir-1	2.370	0.991	1.669	0.988	1.683	0.995	3.706	0.994
D-R	10.555	0.815	4.154	0.936	16.175	0.840	16.401	0.862
Temkin	2.780	0.985	2.500	0.968	2.260	0.995	5.747	0.983

Ar-BGH (0.115 L/g), Kr-GGH (0.0585 L/g), and Ar-RH (0.0865 L/g). The higher magnitude of 'q_m' indicates that the amount of phenol per unit weight of sorbent (to form a complete monolayer on the surface) seemed to be significantly higher. A relatively lower 'b' value (<0.1) implies low surface energy in all the systems, thus, indicating a probable stronger bonding between phenol and sorbents [26]. In fact, fairly low to moderate 'b' values (0.0096–0.0158) have been reported in many of the sorbent–phenol systems, involving palm-seed coat AC bentonite and RH [27–29].

To explain possible multilayer adsorption and non-linear energy distribution for the adsorption sites, the Freundlich isotherm was studied for the same adsorbents. The Freundlich constants 'k_f' and 'n' are the measures of adsorption capacity and intensity of adsorption. The results revealed that the adsorption of phenol on to soil-agro blends sorbent–sorbate system also obey Freundlich adsorption isotherms. Model fits for the Freundlich isotherm model along with experimental data are presented in Figs. 3–6 and Table 2, respectively. Since greater the value of k_f (the Freundlich constant), higher the phenol uptake from the aqueous solution [26,27]. The values of Freundlich isotherm constant k_f value of Kr-BGH blend (22.62), Ar-BGH blend (12.87), Kr-GGH blend (8.739), and Kr-RH blend (7.861). And also compared with that of commercial activated carbon (19.26), the values of Freundlich constant k_f for Kr-BGH blend were high, that indicates a greater affinity for phenol, because of exponential energy distribution. Furthermore, it was observed that, in all these sorbate–sorbent systems, the n values satisfy the condition(s) of heterogeneity [30], that is, $1 < n < 10$ as well as $0 < 1/n < 1$, indicating their agreement to Freundlich isotherm. The Freundlich model predicts that the phenol concentration on the adsorbent will increase as long as there is an increase in the phenol concentration in the liquid phase.

Several researchers had modified the classical Langmuir equation by rearranging the constants without changing the degrees of freedom [31–33]. The modified Langmuir-1 and modified Langmuir-2 models are accounting for temperature variability and heterogeneity of the adsorbent of the system, respectively [34]. The model fits and experimental data as shown in Figs. 3–6 and Table 2, respectively. However, modified Langmuir-1 provided a fit as satisfactory as the Langmuir isotherm equation. The value of exponent term '*n*' is negative for all systems. This indicates that phenol sorption could be favored at high temperature. This result was quite similar to the findings by Singh and Nayak [35] based on their studies of the sorption of phenol by fly ash and impregnated fly ash, in which they reported the increase in sorption of phenol by fly ash with increase in the temperature (in the range of 30°C–50°C).

Therefore, the mechanism of sorption process could be endothermic in nature, indicative of the involvement of several mechanisms in the sorption of phenol. On the other hand, modified Langmuir-2 isotherms totally fail to fit the experimental data for the sorption of phenol onto all systems (soil-agro blend sorption–sorbate system) as shown in Figs. 3–6. Maurya and Mittal [36] observed just the same results during modeling of adsorption equilibrium data for adsorption of dyes on an AC. Application of Dubinin–Radushkevich isotherm, which was mostly used for gas phase adsorption on AC, was also found applicable to the liquid–solid phase adsorption [36,37]. This phase of study involved evaluating the adsorptive capacity using Dubinin–Rdushkevich model applied to study the adsorption of phenol, the model found to fit experimental data (for all adsorbents) fairly well, though not adequate, as shown in Figs. 3–6. The Dubinin–Radushkevich equation could predict relatively nearer values to the experimental data. The poor performance of the Dubinin–Radushkevich equation (except Ar-BGH blend) indicated the contribution of phenol sorption mechanisms other than van der Waals force. However, in the case of sorption of phenol onto Ar-BGH blend, it predicts better, indicating the predominance of the sorption mechanism based on van der Waals forces.

The Temkin isotherm model assumes that adsorption to be characterized by a uniform distribution of binding energies up to some maximum value [36,38]. The non-linear regression analysis to fit the Temkin isotherm model along with experimental data are presented in Figs. 3–6 and Tables 2 and 3, respectively. The results revealed that the characteristic curves of Temkin are very close to the Langmuir, Freundlich, and modified Langmuir-1 curve. This provided no improvement over the Langmuir, Freundlich, and modified Langmuir-1 isotherm model, which is mathematically simple, and more widely used.

3.5.1. Predicting best bi-parameter model isotherm

On comparison of the six non-linearized bi-parameter isotherm models, for all the adsorbents used in this study, it is observed that the Langmuir and modified Langmuir-1, non-linearized isotherm equation showed higher value of correlation coefficient ($r^2 > 0.991$) and lower value of APEs (<3.723) than that of the other four bi-parameter non-linearized isotherm equations as shown in Table 2 and the order of suitability of isotherms as shown in Table 3.

3.6. Three-parameter models

The experimental adsorption data of phenol were also analyzed using the well-known three-parameter non-linearized isotherm models, namely, Langmuir–Freundlich, Fritz–Schlunder, Radke–Prausnitz, Toth, Jossens, Redlich–Peterson, and Sip model. The three-parameter models express the adsorption capacity, q_m, as an inherent function of the equilibrium concentration and are empirical in nature. The model seems to fit well with all the sorbate–sorbent systems (Figs. 7–10 and Table 4). The values of model constants along with corresponding correlation coefficient and APE for all sorbent–sorbate system presented in Tables 4 and 5, respectively. The three-parameter models are empirical in nature and the adsorption capacity, q_m, as an inherent function of the equilibrium concentration. The model seems to fit well for all the sorbate–sorbent systems (Figs. 7–10 and Table 4). The values of model constants along with corresponding correlation coefficient and APE for all sorbent–sorbate system presented in Tables 4 and 5, respectively.

The Langmuir–Freundlich isotherm model includes the characteristics of Langmuir and Freundlich isotherm. The values of the maximum adsorption capacity obtained for all sorbate–sorbent system using the Langmuir–Freundlich isotherm model are higher than those calculated by the Langmuir and Freundlich isotherm models as shown in Tables 4 and 5. Model fits for the Langmuir–Freundlich isotherm model along with experimental data are presented in Figs. 7–10, respectively. The sorption capacities of different sorbent–sorbate system are Kr-BGH soil-agro blend (71.22 mg/g), Kr-GGH soil-agro

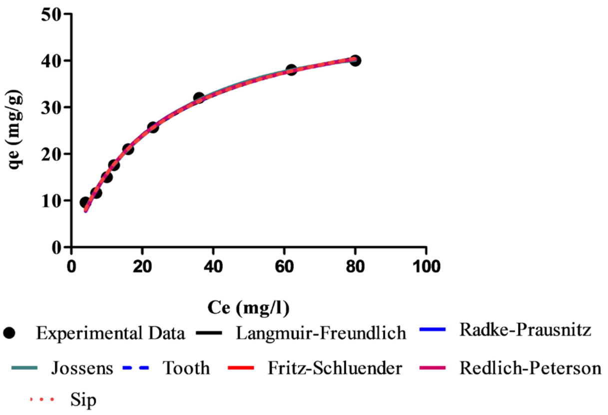

Fig. 7. Three-parameter isotherm models for Kr-BGH.

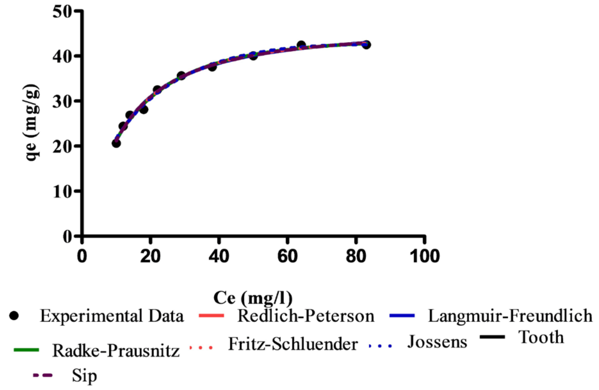

Fig. 8. Three-parameter isotherm models for Ar-BGH.

blend (59.65 mg/g), Ar-BGH soil-agro blend (46.74 mg/g), and Ar-RH soil-agro blend (39.57 mg/g). The Langmuir–Freundlich model is a modified three-parameter version of the Langmuir and Freundlich model, which presented better fit to the experimental data. When compared with two-parameter Langmuir and Freundlich isotherm model the maximum adsorption capacity q_m has increased.

In this work, when Fritz model applied to study adsorption of phenol, for all sorbate–sorbent system, the model found to fit experimental data well, as shown in Figs. 7–10. Fritz–Schlunder isotherm model showing good fit with experimental data, yet with no significant improvement in the model's data fitting. It was observed that the isotherms for all the systems were significantly correlated regarding the three-parameter models.

The experimental data of all the sorbate–sorbent system were found to fit the Radke–Prausnitz isotherm model as good as Langmuir–Freundlich and Fritz non-linear isotherm model as shown in Figs. 7–10. The Sips equation was found to adequately fit the experimental results as shown in Figs. 7–10. The exponent *B* value is in the range of 0.79–0.93 for all sorbate–sorbent system except Ar-BGH soil-agro residue blend system. It means that the adsorption data obtained in this study is more of a Freundlich form. Whereas in the case of Ar-BGH sorbate–sorbent system the exponent *B* value is 1.238, which is in the range of 1. It may be concluded from the adsorption data, it is more of a Langmuir form rather than that of Freundlich form.

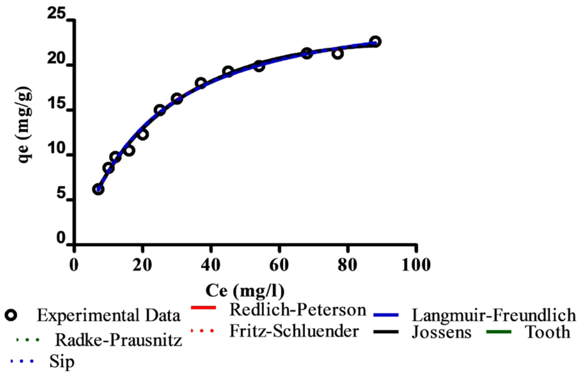

Fig. 9. Three-parameter isotherm models for Ar-RH.

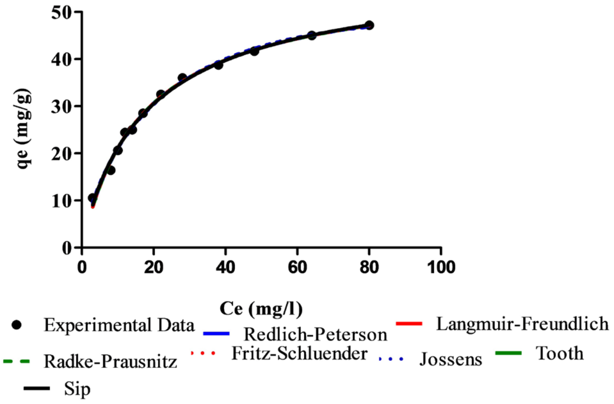

Fig. 10. Three-parameter isotherm models for Kr-GGH.

Table 4
Details of three-parameter isotherm constants for soil and soil-agro blend

Type of isotherm \ type of adsorbent	Kr-soil	Ar-soil	Kr-BGH	Ar-BGH	Kr-GGH	Kr-RH
Langmuir–Freundlich						
q_{mLF}	55.71	37.83	71.22	46.74	59.65	39.57
K_{LF}	0.03635	0.02785	0.1403	0.08605	0.05256	0.07761
mLF	0.9165	0.9044	0.7989	1.238	0.9303	0.9154
r^2	0.9958	0.9988	0.9975	0.9919	0.9939	0.9961
Fritz–Schlunder						
q_{mFS}	43.79	22.9	49.19	81.13	50.22	29
K_{FS}	0.05369	0.05849	0.2848	0.03961	0.06944	0.1284
A	0.9634	0.9138	0.9327	1.105	0.9722	0.94
r^2	0.9953	0.9986	0.9972	0.9919	0.9936	0.9966
Radke–Prausnitz						
q_{mRP}	48.93	25.73	51.11	70.32	53.02	30.3
K_{RP}	0.04652	0.05	0.2581	0.04826	0.06434	0.1189
mRP	0.9717	0.8679	0.9197	1.17	0.9675	0.9147
r^2	0.9953	0.9985	0.997	0.9919	0.9935	0.9967
Toth						
q_{mT}	56.08	39.51	72.67	46.18	59.78	40.56
K_T	0.06649	0.06771	0.3686	0.02293	0.08057	0.1405
mT	0.8718	0.809	0.7167	1.365	0.9023	0.8414
r^2	0.9955	0.9987	0.9975	0.9918	0.9937	0.9963

Table 5
Isotherm parameters (three parameters) average percentage error and correlation coefficients

Adsorbent	Kr-BGH		Ar-BGH		Ar-RH		Kr-GGH	
Isotherm	APE	r^2	APE	r^2	APE	r^2	APE	r^2
Langmuir–Freundlich	1.235	0.998	1.645	0.992	1.887	0.996	3.486	0.994
Fritz–Schlunder	1.258	0.997	1.664	0.992	1.695	0.997	3.632	0.994
Radke–Prausnitz	1.270	0.997	1.666	0.992	1.655	0.997	3.660	0.994
Jossens	1.344	0.997	1.665	0.991	2.690	0.994	3.359	0.994
Toth	1.218	0.998	1.656	0.992	1.811	0.996	3.588	0.994
Redlich–Peterson	1.258	0.997	1.666	0.992	1.655	0.997	3.660	0.994
Sip	1.235	0.998	1.645	0.992	1.887	0.996	3.486	0.994

Redlich–Peterson model has been most frequently used model in liquid-phase adsorption. In most cases the applicability of the Redlich–Peterson isotherm model is compared with only two-parameter isotherm models, namely, Langmuir and Freundlich isotherm models. In this study, the Redlich–Peterson isotherm model has ascertained its capability to fit the experimental data in more accurate ways than all the two-parameter isotherm models as shown in Figs. 7–10.

Toth isotherm [39] has been useful in relating adsorption in heterogeneous systems based on potential theory. It assumes an asymmetrical quasi-Gaussian energy distribution with a widened left-hand side, that is, most sites have adsorption energy less than the mean value. The Toth isotherm model is a further improvement over the Langmuir–Freundlich isotherm model. This reduces to the Henry's law equation at very low concentration and approaches the saturation limit at high concentration [40]. This also showed a better fit than two-parameter isotherm models, but there is no significant improvement compared with the Langmuir–Freundlich isotherm model as shown in Figs. 7–10.

Jossens et al. [41] have found that the isotherm equation gives a good representation of the data for adsorption of phenols and aromatic acids from aqueous solutions on AC at 293 K. However, because equilibrium experiments were done only at room temperature and the equilibrium relation did not approach Henry type even at low concentration. The description of the adsorption isotherms by the model of Jossens is presented in Figs. 7–10. The good fit of the lines to the data was found to give a good representation of the data.

3.6.1. Predicting best three-parameter model isotherm

Seven three-parameter isotherm models were tried in this paper to denote the whole concentration range (Figs. 7–10), for phenol adsorption on soil-agro residue blends (Kr-BGH, Ar-BGH, Kr-GGH, and Ar-RH). Based on APEs and correlation coefficients analyzed the order of suitability of isotherms was found to be (as shown in Table 5) as follows for each adsorbent studied.

3.7. Four- and five-parameter models

The experimental adsorption data of phenol adsorption onto all the sorbate–sorbent systems were also analyzed using the four- and five-parameter non-linearized isotherm models, namely, Fritz–Schlunder, Baudu model and Fritz–Schlunder, respectively. An appropriate fitting of the experimental results of adsorption isotherm is obtained using the four- and five-parameter isotherm models are shown in Figs. 11–14. The values of model constants along with corresponding correlation coefficient and APE for all sorbent–sorbate system presented in Tables 6 and 7, respectively. The four-parameter Fritz–Schluender isotherm model, an empirical one, showed equally good fit to the equilibrium data when compared with the three-parameter isotherm models (Figs. 11–14). To predict chemical heterogeneity of the surface, a model having a greater number of model constants should able to predict better [42].

The Baudu model is presented in Figs. 11–14 and shows the prediction of equilibrium adsorption isotherms of phenol on all sorbate–sorbent system. When compared the Baudu model with standard Langmuir and Freundlich isotherm models, the values of the adsorption capacity are maximum in case of Baudu model.

The adsorption data were analyzed by five-parameter isotherm model of Fritz–Schluender. The Fritz–Schluender data as shown in Figs. 11–14 and results show a good fitting to the model. The values of the maximum adsorption capacity obtained using the Fritz–Schluender model are lower than those calculated by the Langmuir model. At higher liquid-phase concentrations, the Fritz–Schluender can be converted to the Freundlich model (the Fritz–Schluender is reduced to the Langmuir model when the exponents' m_1 and m_2 are equal to unity).

3.7.1. Predicting best four- and five-parameter model isotherm

Two four-parameter and one five-parameter isotherm models were used to represent the adsorption data, as shown Figs. 11–14 and Table 6, for phenol adsorption on soil-agro residue blends (Kr-BGH, Ar-BGH, Kr-GGH, and Ar-RH). On comparison of the two non-linearized four-parameter isotherm models, it is observed that the higher value of correlation coefficient ($r^2 > 0.99$) and two-model has equal value of APEs (<2.766) was observed for all the adsorbents that are used in this study. The study of adsorption equilibrium data for phenol on all sorbate–sorbent system, that is, Kalathur soil and Adhanur soil and as well as soil-agro residue blend (Kr-BGH, Ar-BGH, Kr-RH, and Kr-GGH) using various two, three, four and five well-known isotherm models indicated that higher parameter models seemed to be better options for their modeling in comparison with lower parameter models.

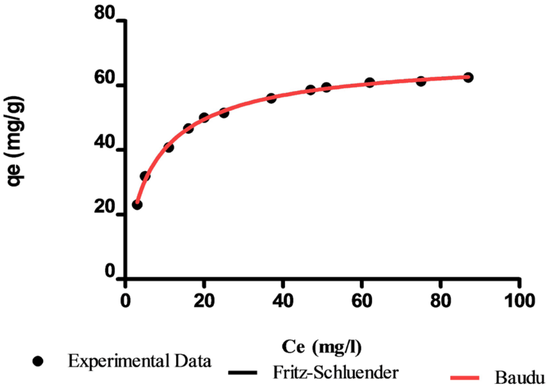

Fig. 11. Four-parameter isotherm models for Kr-BGH.

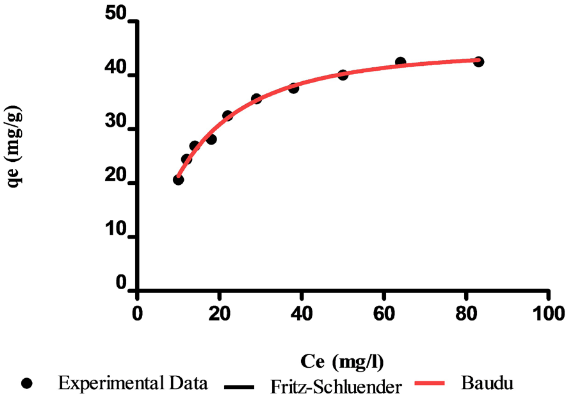

Fig. 12. Four-parameter isotherm models for Ar-BGH.

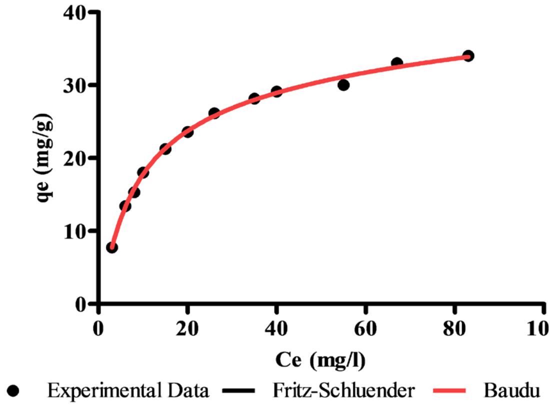

Fig. 13. Four-parameter isotherm models for Kr-GGH.

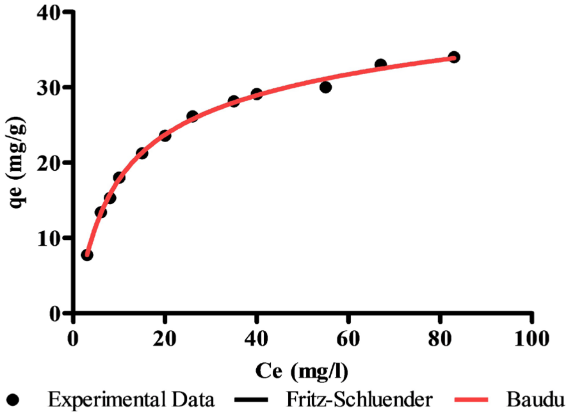

Fig. 14. Four-parameter isotherm models for Kr-RH.

Based on correlation studies and error analysis of the different isotherm models (varying from two- to five-parameter) in relation to the experimental results, the adsorbents (namely, Kr-BGH, Ar-BGH, Kr-RH, and Kr-GGH) were found to exhibit the varying order of suitability. For two-parameter models, the sequence is Langmuir ≥ modified Langmuir-1 > Temkin > Freundlich > Dubinin–Radushkevich > modified Langmuir-2 for all the adsorbents where Freundlich isotherm showed marginally better correlation than Temkin isotherm. However, in the case of three-parameter models, Jossens isotherm was found to be the best for Kr-GGH, but poor for Ar-BGH and Kr-RH.

Langmuir–Freundlich isotherm, on the other hand, shows best correlation for Ar-BGH, relatively lower for Kr-GGH, yet poor correlation for Kr-RH. Toth isotherm was best fitted for Kr-BGH and for all others correlation is average. Although Redlich–Peterson isotherm was found to be best correlated for Kr-RH, but very poor correlation for all other adsorbents. Interestingly, Sip isotherm was not the best suited for any adsorbent, a still fairly good correlation was observed for all adsorbents, except Kr-RH. Both Radke–Prausnitz and Fritz isotherms were poorly correlated with all adsorbents, with slightly better for Kr-RH.

The overall sequence for all the three-parameter isotherms for all adsorbents (taking into account the varying weightage, based on their individual correlation coefficients) was found to be in the following order Langmuir–Freundlich > Sip > Toth > Jossens > Fritz > Redlich–Peterson > Radke–Prausnitz. In case of four-parameter isotherm models, both Fritz and Baudu isotherms show same order of suitability for all the adsorbents studied. The only isotherm used for five-parameter model, that is, Fritz, showed good correlation for all the adsorbents under investigation.

3.8. Overall isotherm model mechanism

The presented models can be broadly classified into two categories. The first includes models that express the adsorption capacity, Q_e, of equilibrium as an implicit function of the equilibrium concentration, C_e (i.e., the Langmuir, Freundlich, Langmuir–Freundlich, and Toth models), while the second expresses adsorption capacity as an explicit function of equilibrium concentration (i.e., modified Langmuir-1, modified Langmuir-2, Temkin, Radke–Prausnitz, Redlich–Peterson, Jossens, Fritz–Schlunder and Baudu models). It is interesting to note that although these models are based on different theoretical concepts, the experimental data appear to fit most of the models. For example, the Langmuir based on monolayer adsorption on a homogeneous surface and the empirically fit. From this investigation, it is evident that these models, although originally developed for gas adsorption on surfaces, could also be employed for adsorption on complex biological surfaces in aqueous solutions. Clearly, it must

Table 6
Details of four- and five-parameter isotherm constants for soil and soil-agro blend

Type of isotherm\ type of adsorbent	Kr-soil	Ar-soil	Kr-BGH	Ar-BGH	Ar-RH	Kr-GGH
Fritz–Schluender						
A	3.495	1.787	14.89	2.89	2.891	4.358
B	0.6583	0.7302	0.1767	0.04348	0.1608	0.0209
α	0.0006	0.0045	0.7441	1.071	1.308	0.7656
β	1.582	1.161	0.7737	1.139	1.156	0.9993
r^2	0.9979	0.9991	0.9975	0.9919	0.9972	0.9945
Baudu						
q_m	202.5	400.2	84.26	2.89	17.98	208.7
bo	0.0208	0.0045	0.1767	23	0.1608	0.02088
x	–0.216	0.1608	–0.2263	–2.139	0.1565	–0.0007
y	–0.151	–0.431	–0.03	1.071	0.1517	–0.2338
r^2	0.9912	0.9991	0.9975	0.9919	0.9972	0.9945

Table 7
Isotherm parameters (four and five parameters) average percentage error and correlation coefficients

Adsorbent	Kr-BGH		Ar-BGH		Kr-RH	
Isotherm	APE	r^2	APE	r^2	APE	r^2
Fritz four	1.228	0.998	1.659	0.992	1.262	0.997
Baudu	1.228	0.998	1.184	0.992	1.237	0.997
Fritz five	0.967	0.998	1.304	0.992	1.198	0.997

therefore be cautioned that the application of these models should be limited only to the mathematical representation of the data and any mechanistic inferences should be very carefully drawn.

3.9. Infrared characterization of adsorbents

The FTIR spectrum of soil-agro residue blend, namely, Kr-BGH and Ar-BGH were analyzed before and after adsorption. The percentage transmission for various wave numbers, absorption bands identified in the spectra and their assignment to the corresponding functional group are presented in Figs. 15–18, respectively. As per studies reported by various researchers [43], agro residues might may be consist mainly of cellulose, hemicelluloses, lignin, pectin, and extractive (fat, waxes, etc.), ions sorb mainly to carboxylic (primarily present in hemicelluloses, pectin, and lignin), phenolic (lignin and extractives) and to some extent hydroxylic (cellulose, hemicelluloses, lignin, extractives, and pectin) and carbonyl groups (lignin, pectin) in the agro residue used, which might be the reason for the presence of complex functional groups observed in FTIR record. Adsorption interaction/reaction of adsorbate over adsorbents is on the basis of the changes in the nature of the specific surface-like participation. On comparing between unloaded adsorbents FTIR and phenol adsorbed adsorbent FTIR, it was observed that there was a shift in wave number of dominant peaks associated with the phenol.

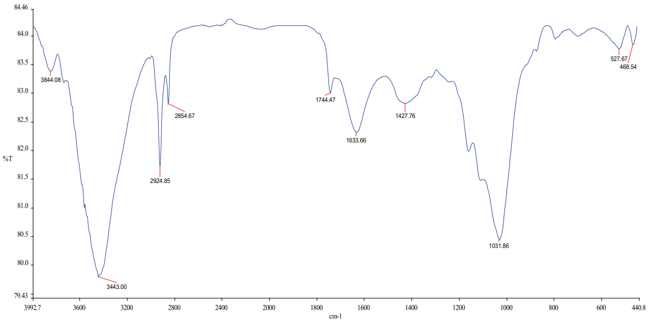

Fig. 15. FTIR analysis of Kr-BGH blend before adsorption.

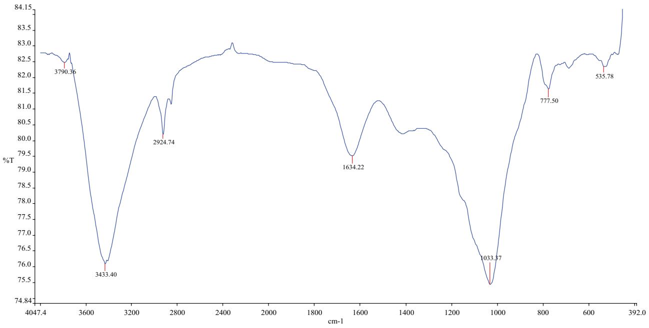

Fig. 16. FTIR analysis of Ar-BGH blend before adsorption.

3.10. Desorption studies

Desorption studies help to elucidate the mechanism of adsorption and recover the precious phenols, water, and adsorbent. Attempts were made to desorb phenol from the spent carbons using sodium hydroxide of various strengths and also by solvent extraction methods [27]. In the first method, NaOH reagent may be attributed to the formation of sodium salt of phenol, which may facilitate desorption of phenol from the adsorbent surfaces at higher pH range [27,44] was found that approximately 0.14 N NaOH is required for quantitative desorption of phenol

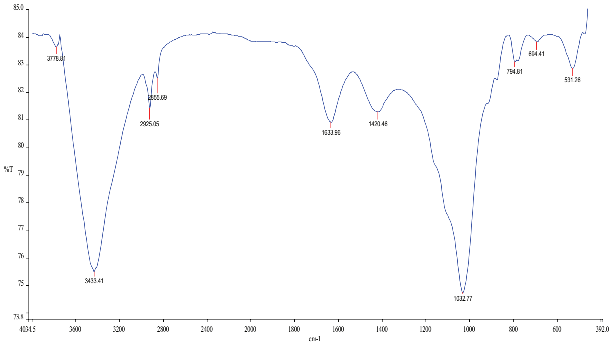

Fig. 17. FTIR spectrum of Kr-BGH soil-agro residue blend after adsorption.

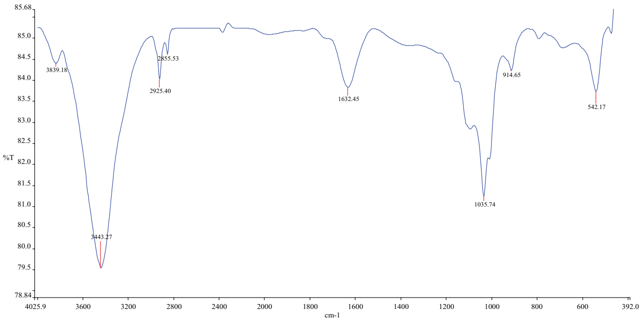

Fig. 18. FTIR spectrum of Ar-BGH soil-agro residue blend after adsorption.

from AC. Srihari and Das [45] found that 0.15 N NaOH is required for quantitative desorption of phenol from carbons prepared with GGH, BGH, and RH, whereas 0.12 and 0.1 N in the case of press mud and Hemidesmus indicus, respectively. The desorbed phenol fraction was 62%, 62%, 62%, and 60% for maximum 0.15 N NaOH elution solution in the case of Kr-soil, Ar-soil, Kr-BGH, Ar–BGH, and Kr-RH soil-agro blend residue.

Results of phenol desorption studies are shown in Fig. 19. The amount of phenol desorbed at the end of the desorption step was quantified. These results along with the amount retained after 160 min of desorption are shown in Fig. 20. For the different adsorbents at an initial concentration of 100 mg/L, actual amounts of recovery ranged from 60% to 64%. This suggests that nearly 40% of the amount adsorbed was retained by the two soils and soil-agro blends. The silt fraction, which accounts for soil-agro residue blends for the lack of complete recovery of the amount sorbed. The lowest measured recovery of the amount desorbed was observed for Kr-RH soil-agro blend. This may be a direct result of the low cellulose and lignin content in the Kr-RH soil-agro blend [46]. These desorption studies clearly indicate considerable hysteresis in soils as well as soil-agro residue blends. This hysteretic behavior resulting from the discrepancy between adsorption and desorption isotherms was not surprising in view of the strong retention behavior of phenol in the present studies. Xue and Selim [47] showed that observed hysteresis from batch experiments is indicative of irreversible adsorption of solutes by the soils matrix.

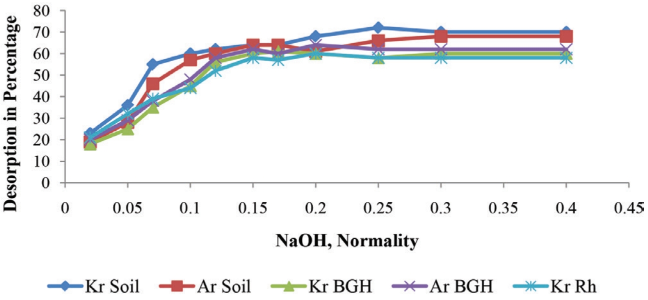

Fig. 19. Desorption studies of adsorbents with various NaOH normality.

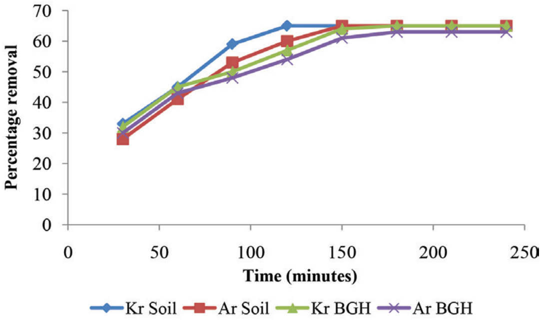

Fig. 20. Percentage of phenol removal vs. time during desorption for soils and soil-agro residue blends with initial concentrations (100 mg/L).

3.11. Biodegradation of adsorbed phenol

Cow dung is basically the digested residue of herbivorous matter which is acted upon by symbiotic bacteria residing within the animal's rumen. The resultant fecal matter is rich in minerals and contains diverse classes of microorganisms. The physicochemical characterization of cow dung microbial consortium indicates the presence of organic carbon, nitrogen, phosphorus, sulfate, calcium, chloride, sodium, potassium, and magnesium in high concentration and these served as nutrients to the microbial consortium. The data indicate the presence of bacteria, fungi, and actinomycetes in cow dung slurry. The presence of nutrients as well as microorganisms in cow dung has been found to have great influence on the bioremediation of phenol. The results of this study demonstrate that cow dung is a potential source of highly effective microbial consortia that can be used in bioremediation of residual phenol present in the soil-agro blend adsorbents.

During biodegradation, the pH varied between 7.3 and 6.8, which is desirable since biodegradation rate is highest at near neutral pH [48]. Dissolved oxygen was found to be decreasing indicating the growth and proliferation of microorganisms [49,50].

The percentage of organic carbon decreased from 0.50% to 0.32% during the experiment. The decrease in percentage organic carbon is one of the key indicators used in bioremediation process. During bioremediation, the chemical oxygen demand (COD) and biological oxygen demand (BOD) were also monitored as indicators of bioremediation and microbial growth (Figs. 21 and 22). Fig. 21 demonstrates the decrease in COD concentration over a period of bioremediation, which

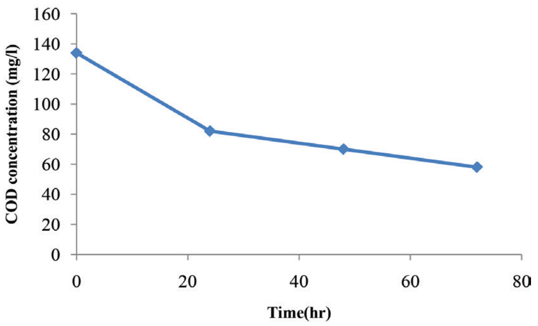

Fig. 21 Chemical oxygen demand (COD) variations during phenol bioremediation by cow dung slurry.

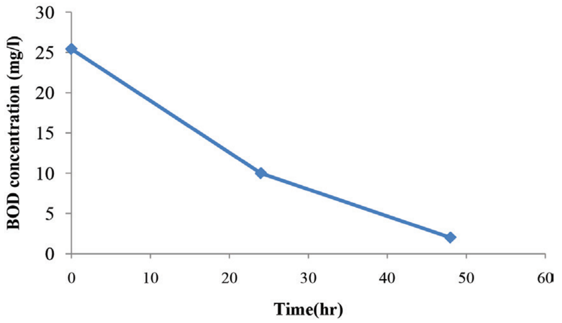

Fig. 22. Biological oxygen demand (BOD) variations during phenol bioremediation by cow dung slurry.

indicates the degradation of phenol by microorganisms present in the cow dung consortium. The decrease in BOD values indicates the growth of microorganisms as shown in Fig. 22. The bioremediation of phenol was carried out using aqueous cow dung slurry directly as a biomass. The interaction of cow dung microflora with the phenol led to the degradation of phenol (35 mg/L concentration) started within 2 h and was degraded below the detected limits of phenol within a period of 10 h (Fig. 22). Clearly, the lag phase at this concentration of residual phenol is very short.

The results of this study demonstrate that cow dung is a potential source of highly effective microbial consortia that can be used in bioremediation of phenol. This potential should be exploited to enhance removal of hazardous compounds from the environment.

4. Conclusions

The batch studies carried out to evaluate adsorption capacities of the blend between three agro wastes (i.e., black gram, green gram, and RH) with Kalathur soil and Adhanur soil were found to show high adsorption (>96%) at room temperature (30°C ± 2°C). The optimized dosages required for adsorption were, respectively, found to be 0.75, 0.9, 0.85, and 1.25 g (for soil-agro blends: KR-BGH, Ar-BGH, Kr-GGH, and AR-RH). In fact, the addition of agro residue to the soil was found to cause a reduction of 11%–25% requirements of adsorbent, in comparison with an adsorbent requirement for use of soil alone. The optimized contact times for all the adsorbents (soil-agro residue blends) were found to be 360 min (on average).

In analyzing all the sorbate–sorbent systems, the higher parameter models seemed to be better options for their modeling in comparison with lower parameter models. Besides, it was also observed that for complex heterogeneous mixtures (such as soil-agro residues blends), the study of higher-parameter models using non-linear analysis seemed to be preferable to lower-parameter models (or even linearized higher parameter models, wherever possible to linearize).

Based on the kinetic reaction, the adsorption was found to favor pseudo-second-order reaction for all adsorbents, indicating this model to be the rate-limiting step. On evaluation of the Elovich kinetic model, the values of the two constants (α and β) showed good linearity (r^2 values varies from 0.931 to 0.9996), and indicated chemisorptions as the primary mechanisms involved in all sorbate–sorbent systems (maximum being the case of Kr-soil).

The FTIR spectrum of soil-agro residue blend (namely, Kr-BGH and Ar-BGH) was fairly heterogeneous as evidenced by different characteristic peaks (with possible presence of phenolic, carboxylic, hydroxyl, and carbonyl groups) and specific changes associated with adsorption as indicated by distinct spectral changes (such as disappearance of some bands, broadening of some bands, and spectral shifts).

The desorption study of phenol from adsorbed adsorbent indicates the optimized duration of desorption of adsorbate as 160 min (with alkali-leaching pretreatment), for the soils and soil-agro residue blend as 3:5. The residual phenol even after desorption was attempted for biodegradation using cow dung (because of its rich possession a wide range of microflora as evaluated by microbial analysis in the laboratory), resulting in degradation of phenol from 35 mg/L to below the detected limits of phenol within a period of 10 h.

The present work is a clear demonstration of the potential for specific soil and agro residue as real robust adsorbents. The entire range of adsorbents studied was eco-friendly and most low-cost effective and interestingly the residual adsorbents were nullified with the practically no cost, most abundant material of India, that is, cow dung. These studies also present scope for exploration of the potentials of low-cost newer agro residue (with possibly natural pretreatments, pelletization, and commercialization).

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