REMOVAL OF PHENOLIC COMPOUNDS FROM AQUEOUS SOLUTIONS BY BIOSORPTION ONTO *ACACIA LEUCOCEPHALA* BARK POWDER: EQUILIBRIUM AND KINETIC STUDIES

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ABSTRACT

The aim of this work is to determine the potential application of *Acacia leucocephala* bark powder as a biosorbent for removing phenolic compounds from aqueous solutions. Experiments were carried out as function of initial pH (2-10), contact time, initial concentration of adsorbate (100–400 mg/L), and effect of adsorbent dosage. Adsorption of phenolic compounds (phenol, 2-chlorophenol (2-CPh) and 4-chlorophenol (4-CPh)) from aqueous solutions on bark powder was studied under batch equilibrium conditions. Maximum phenol removal was observed at pH 7.0. Increase in the pH to above neutrality resulted in the decrease in the phenolic compounds adsorption capacity. The adsorption process was fast, and it reached equilibrium in 4-h contact time. The kinetics study demonstrated that the adsorption process proceeded according to the pseudo-first-order kinetic model. Three isotherm models (Langmuir, Freundlich and Dubinin-Radushkevich) were employed in the analysis of the adsorption equilibrium data. The data fitted well with the Langmuir isotherm. The Langmuir model resulted in the best fit and the new adsorbent had maximum adsorption capacities for phenol, 2-CPh and 4-CPh of 94.33, 147.05 and 181.81 mg/g, respectively. The results indicated that the *A. leucocephala* bark powder could be an alternative for more costly adsorbents used for removal of phenolic compounds from aqueous media.

Keywords: Adsorption, *Acacia leucocephala* bark powder, Phenolic compounds, Kinetics and Isotherm models.

INTRODUCTION

The introduction of toxic pollutants can have a several impact on many organisms that live not only in aquatic ecosystem but also in the body of the human beings.¹ They exist in different concentrations in wastewaters disposed from many industrial processes, including petrochemical industry, coking, synthetic rubber, plastics, paper, oil refineries, as well as phenolic resin industries.^{2,3} Phenol and its derivatives are considered as noxious pollutants, because they are toxic and harmful to living organisms even at low concentrations.⁴ The utilization of phenol contaminated waters causes protein degeneration, vomiting, tissue erosion, smoky colored urine, paralysis of the central nervous system and also damages the kidney, liver and pancreas in human bodies.⁵ According to the recommendation of World Health Organization (WHO), the permissible concentration of phenolic contents in potable waters is 1 µg/L and the regulations by the Environmental Protection Agency (EPA), call for lowering phenol content in wastewaters less than 1 mg/L.^{6,7} Thus, it is fully recommended to removal of phenolic compounds from industrial effluents before entering in to the water stream.

In recent years, interest has been focused on the removal of phenols from aqueous solution. Traditionally, biological treatment, activated carbon adsorption, solvent extraction, chemical oxidation and electrochemical methods are the most widely used methods for removing phenol and phenolic compounds from wastewaters.⁸ Activated carbon is one of the most effective ones, as it has a porous structure and provides a good capacity for the adsorption of organic compounds due to its high surface area.^{9,10} However, activated carbon has a number of disadvantages, such as relatively high cost, expensive cost and considerable loss during chemical or thermal regeneration of spent carbon. This has led many researchers to search for more cost-effective and efficient adsorbents to remove organic contaminants from water and wastewater. Fly ash,¹¹ rice husk,¹² peat,¹³ bentonite,¹⁴ and polymeric adsorbents^{15,16} have been tested for the adsorption of organic pollutants. The search for new and innovative treatment techniques has focused attention on the adsorption capacities of other adsorbents, such as agricultural by-products and lignocellulosic residues,¹⁷⁻¹⁹ which are readily available and do not need to be regenerated due to their low cost. Numerous studies on the sorption of metals and organic pollutants by these alternative adsorbents in batch systems have been reported.^{17,20} Removal of cadmium and mercury ions from aqueous solution by sorption on treated *Pinus pinaster* bark: kinetics and isotherms was studied by Vazquez et al.²¹ Regarding to the sorption of organic pollutants by pine bark reported interesting results for organochlorine pesticides.²² Adsorption of phenol on formaldehyde-pretreated *Pinus pinaster* bark: equilibrium and kinetics was studied by Vazquez et al.²³

Acacia leucocephala bark, agricultural and easily available waste, could be an alternative for more costly wastewater treatment processes. *Acacia leucocephala*'s native range through South and Southeast Asia is noncontiguous. Its largest continuous distribution is arid India through Sri Lanka, Bangladesh, Burma and much of Thailand. *Acacia leucocephala* is an important dry-season fodder and pasture tree throughout its range. Leaves, tender shoots and pods are eagerly eaten by goats, sheep and cattle. All mature *Acacia leucocephala* put on an annual layer of bark, which contributes to the increasing diameter of the stems. In some species the outermost layer dies and is annually deciduous either in long strips or in variably sized flakes. Due to the high number of *Acacia leucocephala* trees in India, massive amount of bark is produced, which is being disposed off as waste. Lignocellulosic wastes materials are available in abundance, renewable and low in cost. The *Acacia leucocephala* bark fulfils these requests its potential has been under estimated. A few studies were published suggesting good efficiencies in heavy metals removal from aqueous solution by *Acacia leucocephala* bark.^{24,25} In the interest of the environment, according to authors' survey, there is no extensive study on the biosorptive removal of phenolic compounds from aqueous solutions using *A. leucocephala* bark biomass in literature. In addition, this material was chosen as novel biosorbent in this study due to being of its naturally abundant, renewable and thus cost-effective biomass.

The aim of this present work is to investigate the biosorption potentiality of *A. leucocephala* bark powder biosorbent material for the removal of phenol, 2-CPh and 4-CPh from aqueous medium. The *A. leucocephala* bark powder was characterized by scanning electron microscopy (SEM). Further this *A. leucocephala* bark powder was characterized before and after adsorption of phenolic compounds by Fourier Transform Infrared (FTIR) spectroscopy studies. The effect of various factors, such as time of contact, biosorbent dosage, pH and initial adsorbate concentrations on this biosorption process was investigated under batch equilibrium technique. Moreover, kinetic and equilibrium models were used to fit experimental data.

MATERIALS AND METHODS

Materials

Acacia leucocephala bark was collected from a local *Acacia leucocephala* tree near Pullampet, Kadapa District, Andhra Pradesh, India, for the preparation of biosorbent. Required raw materials, Phenol (Junsei Chemical Co. Ltd (Tokyo, Japan), 2-CPh and 4-CPh (Junsei Chemicals Co., Korea) were used without further purification. Stock solutions were prepared by dissolving 1.0 g of phenol, 2-CPh and 4-CPh individually in one liter of double distilled water. These stock solutions were used to prepare 100, 200, 300, and 400 mg/L solutions of phenol, 2-CPh and 4-CPh. 0.1 M HCl and 0.1 M NaOH, used

to adjust pH, were obtained from Samchun Chemicals, South Korea. Water used for preparation of solutions and cleaning adsorbents was generated in the laboratory by double distilling the deionized water in a quartz distillation unit.

Preparation of biosorbent

Acacia leucocephala bark was thoroughly washed with distilled water to remove mud and dirt. Then *A. leucocephala* bark powder was soaked in 0.1M NaOH to remove lignin based color materials followed by 0.1M H₂SO₄. Finally it was washed with distilled water several times and dried in an oven at 80°C for 6 h and cooled at room temperature in desiccators. The physical, chemical and surface characterization of *A. leucocephala* bark powder is carried out using standard methods and the results are given in Table 1. The dried *A. leucocephala* bark powder was stored in desiccators until used. The dried bark was ground to fine powder and used as biosorbent without any pretreatment for phenolic compounds adsorption.

Table 1. Physical, chemical and surface characterization of *Acacia leucocephala* bark powder.

Parameter	Value
Color	Light Yellowish
Odour	None
Weight loss (%)	54.8
Apparent (bulk) density (g/cm ³)	0.251
Moisture content (%)	7
Ash content (%)	4.88
BET Surface are (m ² /g)	0.27
Carbon (%)	44.8
Hydrogen (%)	5.65

Analysis of phenolic compounds

The concentration of phenol, 2-CPh and 4-CPh, in aqueous medium was determined by measuring absorbance at wavelengths of 270 nm, 274 nm and 280 nm, respectively, Using UV-Spectrophotometer (Shimadzu UV-1601 Spectrophotometer, Japan). In order to reduce measurement errors in all the experiments, UV absorption intensity of each solution sample was measured in triplicates and the average value was used to calculate the equilibrium concentration based on standard calibration curve, whose correlation coefficient square (R²) was 0.999. The experimental error was observed to be within ±2%.

Batch studies

Adsorption experiments were conducted by varying pH, contact time, adsorbent dosage and adsorbate concentration. In adsorption equilibrium, experiments were conducted in a set of 125mL Erlenmeyer flasks, where solutions of phenolic compounds 100 mL (phenol, 2-CPh and 4-CPh) with different initial concentrations (100–400 mg/L) were added in these flasks. The pH of solution was maintained at a desired value by adding 0.1 M NaOH or HCl. Equal masses of 0.4g/0.1L of *A. leucocephala* bark powder were added to phenolic compounds solutions and each sample was kept in a shaking Water Bath Temperature controller of 220 rpm at 25±1°C for 4h to reach equilibrium of the solid–solution mixture. Samples were taken out from flasks and the solutions were separated from the adsorbent by filtered through Whatman No.50 filter paper (2.7 µm size particle retention) to eliminate any fine particles. Then the concentration of phenolic compounds was determined by measuring absorbance using UV-Vis spectrophotometer (Shimadzu UV/Vis-1601 Spectrophotometer, Japan) at 270 nm, 274 nm and 280 nm for phenol, 2-CPh and 4-CPh, respectively. The amount of adsorption at equilibrium, q_e (mg/g) and the percent adsorption (%) was computed as follows:

$$q_e = \frac{(C_0 - C_{eq})V}{m} \quad (1)$$

$$\text{Percent adsorption } (\%) = \frac{C_0 - C}{C_0} \times 100 \quad (2)$$

where C_0 and C_{eq} (mg/L) are the liquid-phase concentrations of phenolic compounds at initial and equilibrium, respectively. V (L) is the volume of the solution, m is the mass (g) of the bark powder and C the phenolic compounds concentrations at the end of adsorption.

The procedures of kinetic experiments were basically identical to those of equilibrium tests. The aqueous samples were taken at preset time intervals

and the concentrations of phenolic compounds were similarly measured. The amount of adsorption at time t , q_t (mg/g), was calculated by

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (3)$$

RESULTS AND DISCUSSION

Characterization of acacia leucocephala bark powder Fourier Transform Infrared (FTIR) Studies

Characterization of the biosorbent was carried out by Fourier Transform Infrared Spectroscopy to determine the type of functional groups on the biosorbent. FTIR spectra in the range of 4000–400 cm⁻¹ for the pure *Acacia leucocephala* bark powder and the *A. leucocephala* bark powder loaded with phenol, 2-CPh and 4-CPh are shown in Fig. 1(a), (b), (c) and (d), respectively. The spectra display a number of absorption peaks, indicating the complex nature of the biosorbent material examined. Fig. 1(a)–(d) shows the FTIR spectra had a broad band absorption peaks at 3426 cm⁻¹ corresponding to the overlapping of –OH and –NH peaks. On the other hand, the two peaks appear at 2918–2850 cm⁻¹ which represent the asymmetrical and symmetrical stretching vibration of methylene (–CH₂) group, respectively. The C=O stretching of *A. leucocephala* pure bark powder as at 1613.8 cm⁻¹. The presence of –C–O and –C–N linkages are confirmed from the peaks at 1321.7 and 1033.2 cm⁻¹. As we observe in Figure 1(b), (c) and (d), a significant difference can be seen in the FTIR spectra of biosorbent before and after adsorption. The FTIR band of C=O stretching shifted to higher frequency due to involvement of carboxyl (–C=O) group in the adsorption process of phenolic compounds with pure bark powder. This shift and/or broadening of some of the FTIR spectral peaks of the biosorbent in the presence of the phenolic compounds studied provides a clear indication that the functional groups like –NH₂, –OH and –C=O present on the *A. leucocephala* bark powder surface are involved in phenol, 2-CPh and 4-CPh adsorption.

Figure 1. FTIR spectra of phenolic compounds. (a) before biosorption of *Acacia leucocephala* bark powder (b) after phenol biosorption (c) after 2-CPh biosorption (d) after 4-CPh biosorption.

Scanning electron microscopic (SEM) Studies

For morphological characteristics SEM of adsorbent *A. leucocephala* bark powder was carried out. Scanning Electron Microscopy (SEM; Model Evo15, Carl Zeiss, England) is widely used to study the morphological features and surface characteristics of the biosorbent material. In the present study, Scanning electro-micrographs (SEM) show the surface texture and morphology of the biosorbent (Fig. 2a-b). It is evident from the micrograph that the biosorbent has a well-defined rod clusters in net/mat format (500×). At 2.50× magnification, the adsorbent have irregular structure, thus makes possible for the adsorption of phenolic compounds on different parts of the adsorbent.

Figure 2. Scanning electron micrographs of the *Acacia leucocephala* bark powder at (a) 500x and (b) 2.50x magnification.

Effect of pH

The solution pH is one of the dominant parameters controlling biosorption. Phenolic compounds biosorption onto *A. leucocephala* bark powder as a function of pH ranging from 2.0 to 10.0 are given in Fig. 3. The removal of phenolic compounds by *A. leucocephala* bark powder was highly dependent on pH. In order to optimize the pH for maximum removal efficiency, experiments were conducted in the pH range from 2.0 to 10.0 using 0.2 g of *A. leucocephala* bark powder with 100 ml of 100 mg/L initial phenolic compounds concentrations at $25 \pm 1^\circ\text{C}$. In the alkaline range, the pH was varied using aqueous 0.1 M NaOH, whereas in the acidic range, pH was varied using 0.1M HCl. The FTIR spectroscopic analysis showed that the *A. leucocephala* bark powder has a variety of functional groups, such as carboxyl, hydroxyl and amine and these groups are involved in almost all potential binding mechanisms. Moreover, depending on the pH values of the aqueous solutions these functional groups participate in phenolic compounds bindings. The maximum adsorption capacities increase with increase in pH up to pH 7 and decreases there on. It was observed that the relative amount of phenolic compounds adsorbed was significantly affected by pH. The maximum adsorption occurs at neutral pH. Significant decline in removal efficiency was observed for further increase in pH, which may be attributed to formation of phenolate anions. The phenolic compounds considered in this study, viz. phenol, 2-CPh, and 4-CPh, have pKa values of 9.9, 8.3, and 9.2, respectively. When the pH of a solution goes beyond the pKa, phenols chiefly exist as negative phenolate ions, whereas they exist as neutral molecules below the pKa. Due to the electron rich nature of the oxygen atom in phenolate ions, the hydrogen bonding efficiency decreases. Therefore, phenols effectively adsorbed on to the adsorbent as molecules but not phenolate ions. From the experimental results, pH 7.0 was selected as an optimum pH value.

Figure 3. Effect of pH on the biosorption of (□) phenol, (◇) 2-CPh and (▲) 4-CPh onto *Acacia leucocephala* bark powder. Experimental conditions: for phenolic compounds: initial concentrations= 100 mg/L, contact time 5h, biosorbent dosage=0.2g/0.1 L, Temp = $25 \pm 1^\circ\text{C}$, agitation rate 220 rpm.

Effect of biosorbent dosage

The adsorption of phenol 2-CPh and 4-CPh on *A. leucocephala* bark powder were carried out at different adsorbent dose by keeping other parameters constants. The relationship between adsorbent dose and substrate removal for same initial concentrations of phenolic compounds is presented in Fig. 4a-c, respectively. It can be seen from Figures that percentage removal of phenol, 2-CPh and 4-CPh increased with the increase in adsorbent dose while loading capacity, q_e (mg/g), (amount of phenol, 2-CPh and 4-CPh loaded per unit weight of adsorbent) gradually decreased for the same. This increase in loading capacity is due to the availability of higher number of solutes (phenol, 2-CPh and 4-CPh) per unit mass of adsorbent, i.e. higher solute/adsorbent ratio. These experiments were performed with initial concentration of 100 mg/L of solutes and neutral pH of the solution. It can also be seen from these Figures that the uptake of solute markedly increased up to adsorbent dose of 0.4g/0.1L and thereafter no significant increase was observed. It can be concluded that the rate of phenolic compounds binding with adsorbent increases more rapidly in the initial stages and after some point the adsorption is marginal and becomes almost constant. Therefore, the optimum biosorbent dosage was taken as 0.4g/0.1L for further experiments.

Figure 4. Effect of biosorbent dosage level on the biosorption of (a) phenol, (b) 2-CPh, and (c) 4-CPh onto *Schizophyllum commune* fungus [% removal of phenol, 2-CPh, 4-CPh and biosorption capacity (mg/g)]. Experimental conditions: for phenolic compounds: initial concentrations= 100 mg/L, biosorbent dosage = 0.1 - 0.9g, contact time 5h, Temp =25±1°C, pH 7.0.

Effect of contact time and initial concentration

The effect of agitation time on the extent of adsorption of phenolic compounds at different concentrations is shown in Figures 5, 6 and 7 for phenol, 2-CPh and 4-CPh, respectively. Effect of shaking time on biosorption of phenolic compounds onto *A. leucocephala* bark powder was studied over a shaking time of 30–300 min, using 0.4g/0.1L of *A. leucocephala* bark powder, 100–400 mg/L of phenolic compounds concentration at pH 7.0, 25±1°C and 220 rpm shaking speed. The saturation curves rise sharply in the initial stages, indicating that there are plenty of readily accessible sites. Eventually, a plateau is reached in all curves indicating that the adsorbent is saturated at this level. It can be seen from Figures that the contact time needed for phenol solutions with initial concentrations of 100–400 mg/L to reach equilibrium was 4 h. Almost, no remarkable improvement was observed after longer contact time. After this equilibrium period, the amount of solute adsorbed did not change significantly with time, indicating that this time is sufficient to attain equilibrium for the maximum removal of phenolic compounds from aqueous solutions by *A. leucocephala* bark powder. So, the optimum contact time was selected as 4h for further experiments. However, for adsorbate solutions with higher initial concentrations, lower equilibrium times were required. It was also seen that an increase in initial adsorbates solution concentrations resulted in increased phenolic compounds uptake. The removal curves are single, smooth and continuous, indicating the formation of monolayer coverage of the phenol molecules onto the outer surface of the adsorbent.

Figure 5. Effect of contact time on phenol biosorption [Different initial phenol concentrations. (◻) C_0 = 100 mg/L, (●) C_0 = 200 mg/L, (▲) C_0 = 300 mg/L, (◑) C_0 = 400 mg/L; pH = 7.0; biosorbent dosage = 0.4g/0.1 L; contact time 4h, agitation rate: 220 rpm, Temp =25±1°C]

Figure 6. Effect of contact time on 2-chlorophenol biosorption [Different initial 2-CPh concentrations. (◻) C_0 = 100 mg/L, (●) C_0 = 200 mg/L, (▲) C_0 = 300 mg/L, (◑) C_0 = 400 mg/L; pH = 7.0; biosorbent dosage = 0.4g/0.1 L; contact time 4h, agitation rate: 220 rpm, Temp =25±1 °C]

Figure 7. Effect of contact time on 4-chlorophenol biosorption [Different initial 4-CPh concentrations. (◻) C_0 = 100 mg/L, (●) C_0 = 200 mg/L, (▲) C_0 = 300 mg/L, (◑) C_0 = 400 mg/L; pH = 5.0; biosorbent dosage = 0.4g/0.1 L; contact time 4h, agitation rate: 220 rpm, Temp =25±1 °C].

KINETIC STUDIES

Adsorption kinetics has been proposed to elucidate the adsorption mechanism. The kinetic adsorption data were investigated to understand the dynamics of the adsorption process in terms of the order of the rate constant. Different kinetic models including the pseudo-first-order and pseudo-second-order and were applied for the experimental data to predict the adsorption kinetics.

The comparison was done in between the experimental data, calculated data and the regression coefficient (R^2). The well known pseudo-first order and pseudo-second order models were employed to fit the data. It may be represented as,^{26,27}

$$\text{pseudo-first order model : } \log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (4)$$

$$\text{pseudo-second order model : } \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t \quad (5)$$

Where q_t is the amount adsorbed at time t , k_1 and k_2 are the kinetic parameters to be determined. The slope and intercept of plot of $\log(q_e - q_t)$ versus t were used to determine the pseudo-first order rate constant k_1 . The slope and intercept of plot of t/q_t versus t were used to calculate the pseudo-second order rate constant k_2 . The kinetic parameters are included Table 2. The correlation coefficient (R^2) is relatively too low which may be indicative of a bad correlation. In addition, $q_{e, \text{cal}}$ determined from the model is not in a good agreement with the experimental value of $q_{e, \text{exp}}$. Therefore, the adsorption of phenolic compounds onto *A. leucocephala* bark powder is not suitable for the pseudo-second order reaction. Based on higher correlation coefficients and agreement between experimental and calculated q_e values are closer to unity for pseudo-first-order kinetic model; therefore, the biosorption kinetics could well be approximated more favorably by pseudo-first order kinetics model rather than pseudo-second order kin. In order to quantitatively compare the applicability of each model, a normalized standard deviation Δq (%) was calculated.

Table 2. Biosorption rate constants of phenolic compounds on *Acacia leucocephala* bark powder.

	pseudo-first order kinetic model					Pseudo-second order kinetic model			
Phenol									
(mg/L)	$q_{e, \text{exp}}$ (mg/g)	k_1 (min ⁻¹)	$q_{e, \text{cal}}$ (mg/g)	R ²	Δq (%)	$q_{e, \text{cal}}$ (mg/g)	k_2 (g.mg ⁻¹ min ⁻¹)	R ²	Δq (%)
100	67.34	0.0089	65.42	0.9985	0.0135	97.08	7.442 X 10 ⁻⁵	0.9888	3.2507
200	113.99	0.0082	113.13	0.9975	0.0009	163.93	3.887 X 10 ⁻⁵	0.9985	3.1989
300	137.31	0.0085	136.95	0.9977	0.0001	200.54	3.212 X 10 ⁻⁵	0.9990	3.4740
400	154.68	0.0087	155.09	0.9999	0.0001	232.55	2.660 X 10 ⁻⁵	0.9975	4.2239
2-CPh									
100	76.62	0.0117	78.46	0.9992	0.0096	108.69	8.281 X 10 ⁻⁵	0.9973	2.9198
200	134.92	0.0119	137.87	0.9994	0.0079	200.23	3.661 X 10 ⁻⁵	0.9838	3.8778
300	166.98	0.0099	169.86	0.9988	0.0049	250.16	2.782 X 10 ⁻⁵	0.9940	4.1198
400	186.65	0.0094	188.45	0.9848	0.0015	263.15	2.854 X 10 ⁻⁵	0.9932	2.7997
4-CPh									
100	85.92	0.0103	85.20	0.9920	0.0011	114.94	8.097 X 10 ⁻⁵	0.9734	1.9048
200	144.36	0.0105	146.85	0.9976	0.0049	222.25	3.098 X 10 ⁻⁵	0.9714	4.8519
300	174.32	0.0103	175.67	0.9913	0.0010	232.55	3.935 X 10 ⁻⁵	0.9885	1.8597
400	198.77	0.0108	202.72	0.9932	0.0065	270.27	3.409 X 10 ⁻⁵	0.9939	2.1565

$$\Delta q(\%) = 100 \times \sqrt{\frac{\sum [(q_{\text{exp}} - q_{\text{cal}}) / q_{\text{exp}}]^2}{(n-1)}} \quad (6)$$

where the subscripts 'exp' and 'cal' refer to the experimental and calculated values, respectively and n is the number of data points. The lower the value of Δq (%) the model is a better fit for the data. The calculated rate constants for the models, their corresponding regression (R^2) and normalized standard deviation values are listed in Table 2. The results suggest that the higher R^2 values obtained with the pseudo-first order kinetic model, lower Δq (%) values and the calculated q_e (cal) values are closer to the experimental data than the calculated values of pseudo-second order kinetic model. From this observation it may be concluded that the adsorption of phenol, 2-CPh and 4-CPh compounds on the *A. leucocephala* bark powder follows pseudo-first order kinetics.

ADSORPTION ISOTHERM MODELS

Adsorption isotherm is basically important to describe how adsorbate interacts with adsorbents and is critical in optimizing the use of adsorbents. Although several isotherm equations are available due to their simplicity, three well-known models, Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm models were chosen in this study for evaluating the relationship between the amount of phenolic compounds adsorbed onto *A. leucocephala* bark powder and its equilibrium concentration in aqueous solution.

The Langmuir model assumes that adsorption takes place at specific homogeneous sites on the surface of the adsorbent and also, when a site is occupied by an adsorbate molecule, no further

adsorption can take place at this site. The linear form of the Langmuir isotherm can be represented by the following equation,²⁸

$$\frac{1}{q_e} = \frac{1}{Q^0} + \left(\frac{1}{bQ^0}\right)C_e \quad (7)$$

where C_e (mg/L) is the equilibrium concentration of the adsorbate, q_e (mg/g) is the amount of adsorbate adsorbed per unit mass of adsorbent, Q^0 and b are Langmuir constants related to adsorption capacity and rate of adsorption, respectively. The linear plot of $1/q_e$ versus $1/C_e$ indicates that adsorption obeys the Langmuir model.

The most important characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless separation factor (R_L) which is defined as,²⁹

$$R_L = \frac{1}{1 + bC_0} \quad (8)$$

where C_0 (mg/L) is the initial amount of adsorbate and b (L/mg) is the Langmuir constant described above. The R_L parameter is considered as more

reliable indicator of the adsorption. The value of R_L indicates the type of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The value of R_L is less than 1 and great than 0, suggesting the favourable uptake of phenol, 2-CPh and 4-CPh compounds by *A. leucocephala* bark powder.

The Freundlich isotherm is given as,

$$q_e = K_F C_e^{1/n} \quad (9)$$

where K_F ((mg/g)(L/mg)^{1/n}) is roughly an indicator of the adsorption capacity and (1/n) of the adsorption intensity. Value of $n > 1$ represents a favorable adsorption condition.³⁰ The linear form of Eq. (9) is

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \quad (10)$$

which will have a straight line with a slope of 1/n and an intercept of $\ln(K_F)$ when $\ln(q_e)$ is plotted against $\ln(C_e)$.

Another model for the analysis of isotherms of a high degree of rectangularity is Dubinin–Radushkevich isotherm has the following form,³¹

$$q_e = q_s \exp(-B \varepsilon^2) \quad (11)$$

where q_s is the Dubinin–Radushkevich monolayer capacity (mg/g), β a constant related to sorption energy, and ε is the Polanyi potential which is related to the equilibrium concentration as follows

$$\varepsilon = RT \ln \left[1 + \frac{1}{C_e} \right] \quad (12)$$

where R is the gas constant (8.314 J/mol K) and T is the absolute temperature. The constant B gives the mean free energy E of adsorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution and can be computed by using the relationship:

$$E = \frac{1}{\sqrt{2B}} \quad (13)$$

A plot of $\ln(q_e)$ versus ε^2 enables the constants q_s and E to be determined. The parameters of the three isotherms were computed and listed in Table 3. Since the value of R^2 nearer to 1 indicates that the respective equation better fits the experimental data. The experimental data yielded excellent fits within the following isotherms order: Langmuir > Freundlich > Dubinin–Radushkevich, based on its R^2 values. All the evaluated equilibrium models gave good fit to the experimental data, it can be concluded that the Langmuir is the best model describing adsorption of phenolic compounds on the *A. leucocephala* bark powder, as it gave the maximum R^2 value among the considered models. The comparison of maximum monolayer adsorption capacities of different adsorbents obtained from different sources are listed in Table 4 along with the values obtained in the present study.

Table 3. Isotherm Parameters of Langmuir, Freundlich and D-R isotherms for biosorption of phenol, 2-CPh and 4-CPh on *Acacia leucocephala* bark powder

Isotherm model	Adsorbates		
	Phenol	2-CPh	4-CPh
Langmuir			
Q^0	94.33	147.05	181.81
b	0.0509	0.0283	0.0385
R^2	0.9985	0.9941	0.9975
Freundlich			
K_F	6.0201	4.5540	7.1203
n	1.4662	1.1976	1.1767
R^2	0.9793	0.9827	0.9880
Dubinin-Radushkevich			
q_s	3.9018	4.0985	4.1233
E	28.86	25	40.82
R^2	0.8543	0.8527	0.8091

Table 4. Maximum Adsorption Capacities, Q^0 (mg/g), for the Adsorption of Phenol, 2-CPh and 4-CPh compounds by Various Adsorbents.

Sorbent	Adsorbates, Q^0 (mg/g)			References
	Phenol	2-CPh	4-CPh	
Organomified bentonite	333	-	-	14
Bentonite & Perlite	-	-	10.63 & 5.84	32
manganese nodule leached residue	28.50	-	-	33
Sugarcane bagasse fly ash	23.83	-	-	34
Brown alga Sargassum muticum	4.6	79.0	251.0	35
CS/Ab blended beads	156	204	278	36
Date Seed Carbon	138.88	-	-	37
Activated sewage sludge	29.46	-	-	38
commercial activated carbon	49.72	-	-	39
CS/CA blended beads	109	97	-	40
fly ash	3.85	-	-	41
Rice husk char	7.91	-	36.23	42
<i>A. leucocephala</i> bark powder	94.33	147.05	181.81	Present study

CONCLUSIONS

The present work elucidates that the *A. leucocephala* bark powder has proven to be a promising material for the removal of phenol and its derivatives from aqueous medium.

- The pH played an obvious effect on the phenolic compounds biosorption capacity onto *A. leucocephala* bark powder. An increase of the solutions pH leads to a significant increase in the biosorption capacities of phenolic compounds on the *A. leucocephala* bark powder, maximum biosorption capacity occurred at neutral pH.
- The results showed that the good correlation coefficients and the agreement between experimental and calculated values of q_e and lower Δq (%) values showed that the phenolic compounds adsorption followed pseudo-first-order kinetics.
- Biosorption equilibrium data was better described by the Langmuir isotherm model than the Freundlich and D–R adsorption isotherm model.
- The *A. leucocephala* bark powder showed a high adsorption capacity of phenol, 2-CPh and 4-CPh (94.33 mg/g, 147.05 mg/g and 181.81 mg/g) revealing that *A. leucocephala* bark powder could be employed as a promising biosorbent for removal of phenolic compounds adsorption.

All the above results suggested that the *A. leucocephala* bark powder is an effective and alternative biosorbent, but also it is highly efficient for removal of phenol, 2-CPh and 4-CPh compounds from aqueous medium in terms of high adsorption capacity, economically viable; abundantly and locally available.

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