

Biosorption of Phenolic Compounds from Aqueous Solutions using Pine (*Pinus densiflora Sieb*) Bark Powder

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The present study describes the development of a new bioadsorbent from lignocellulosic wastes of agricultural origin. The biosorption capacity of an agricultural solid waste, pine bark (*Pinus densiflora* Sieb.), to remove phenolic compounds (phenol, 2-chlorophenol (2-CPh), and 4-chlorophenol (4-CPh)) from aqueous solutions under batch equilibrium conditions was investigated. The morphological characteristics of the biosorbent were evaluated by BET surface area analysis, Fourier transform infrared spectroscopy (FTIR), elemental analysis, an X-ray diffractometer (XRD), and a scanning electron microscope (SEM). Batch experiments were conducted to investigate the effect of initial pH (2 to 10), contact time, initial concentration of adsorbate (50 to 200 mg/L), and biosorbent dosage. The biosorption of phenolic compounds decreased with increasing pH, and the highest biosorption capacity was achieved at a pH of 6.0. Biosorption equilibrium was established in 120 min. The biosorption equilibrium data were fitted and analyzed with Langmuir, Freundlich, and Dubinin-Radushkevich isotherm equations, as well as four adsorption kinetic models. The kinetics data fitted well into the pseudo-second-order kinetic model, with a correlation coefficient greater than 0.993. The maximum monolayer biosorption capacity of pine bark for phenol, 2-CPh, and 4-CPh was found to be 142.85, 204.08, and 263.15 mg/g, respectively, as calculated by the Langmuir model at 30 ± 1 °C. Pine bark could be used as a new effective, low-cost biosorbent material with good uptake capacity and rapid kinetics for the removal of phenolic compounds from aqueous media.

Keywords: Biosorption; Pine bark powder; Phenolic compounds; Kinetics and isotherm models

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INTRODUCTION

Phenols and chlorophenols are contaminants in soils, sediments, surface waters, and groundwater, because of their worldwide utilization in the last 50 years. In recent years, there have been increasing environmental and toxicological interests about phenolic pollutants due to their widespread occurrence and relative frequency in the aquatic environment (McKinney *et al.* 2006; Zeng *et al.* 2008). The main sources of phenol and chlorophenols are refineries, petrochemical industries (Kumar *et al.* 2011; Sanjay *et al.* 2008), industrial resins, plastics, adhesives, rubber, iron, steel, aluminum, pulp and paper industries, pesticides, fungicides, bactericides, herbicides, medical and health products (including oils, softeners, mouthwash, and eye and ear drops), tannins, electrical industries, and paint industries (Kumar *et al.* 2009a; Srivastava *et al.* 2006; Verschueren 2009).

Phenol and its derivatives are considered noxious pollutants because they are toxic and harmful to living organisms, even at low concentrations. Phenol is a colorless solid and easily miscible in water, so it cannot be identified in water through the naked eye. The United States Environmental Protection Agency (USEPA) has listed phenolic compounds as priority compounds. Stringent US Environmental Protection Agency (EPA) regulation calls for lowering phenol content in the wastewater to less than 1 mg/L (Banat *et al.* 2000). The utilization of phenol-contaminated waters causes protein degeneration, vomiting, tissue erosion, smoky colored urine, paralysis of the central nervous system, and damage to the kidney, liver, and pancreas in human bodies (Knop and Pilato 1985). Because of the low biological degradability, high toxicity, and high ecological persistence of phenolic compounds, wastewater containing phenolic compounds must be treated before being discharged to receiving media (Bayramoglu *et al.* 2009).

To keep waters free from phenol compounds, various processes have been employed for the removal of phenols from aqueous media, including chemical oxidation (He *et al.* 2009), membrane filtration (Kujawski *et al.* 2004), biodegradation (El-Naas *et al.* 2009), electro coagulation (Ugurlu *et al.* 2008), photo degradation (Gomez *et al.* 2011), solvent extraction (Xu *et al.* 2006), and adsorption (Yang *et al.* 2008). Among these methods, adsorption is still the most popular and widely used technique for phenol removal because of its simple design, easy operation, and relatively simple regeneration (Nevskaya *et al.* 2004). This has led many researchers to search for more cost-effective and efficient adsorbents to remove organic contaminants from water and wastewater. Fly ash (Aziz *et al.* 2014; Batabyal *et al.* 1995), rice husk (Mona *et al.* 1997), peat (Viraraghavan and Alfaro 1998), bentonite (Senturk *et al.* 2009), and polymeric adsorbents (Li *et al.* 2002; Pan *et al.* 2005) have been tested for the adsorption of organic pollutants. Currently, very innovative and cost effective methods are used for the removal of toxic substances from waste waters.

Biosorption, as an efficient, cost-effective, and environmentally friendly technique for heavy metals and various organic pollutants, has emerged as a potential alternative to conventional techniques (Febrianto *et al.* 2009). 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 (Garg *et al.* 2009; Rao and Viraraghavan 2002), which are readily available and do not need to be regenerated due to their low cost. Recent studies on the sorption of metals and organic pollutants can be removed using plant materials such as *Acacia leucocephala* bark (Kumar and Min 2011b; Kumar *et al.* 2012), *Pinus pinaster* bark (Vazquez *et al.* 2002), pine bark (Bras *et al.* 1999), formaldehyde pretreated *Pinus pinaster* bark (Vazquez *et al.* 2007), and lignocellulosic substrate extracted from wheat bran (Dupont *et al.* 2003).

Pine bark, an agricultural and easily available solid waste, could be an alternative for more costly wastewater treatment processes. Pine (*Pinus densiflora*) belongs to the family Pinaceae and is widely distributed around the world, including East-Asian countries such as Korea, Japan, and China. Pine is a popular lumber for furniture, paper, plywood, and crafts. It is a soft wood and can dent or scratch easily, making it more popular for house framing and plywood than for fine furniture. Most utility poles are also pine trees. It can be burned for fire wood, especially when a quick fire is needed, as in cooking or a fire pit. The majority of the waste bark is used as a low-grade thermal fuel. The bark is a waste product that has a variety of uses. All mature pine trees 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.

Because of the large number of pine trees in Korea, a massive amount of bark is produced, which is disposed of as waste. Lignocellulosic wastes such as tree bark, lignin, wood, conifer leaves, sawdust, peanut skin, and hull have been considered low-cost and popular biosorbents to remove metals from wastewater, as these wastes are readily available in bulk at almost no cost (Aoyama *et al.* 2000; Sciban *et al.* 2007; Shukla *et al.* 2005). Pine bark can be an attractive and important biomass resource, accounting for about 10 to 15% of the total tree weight (Kofujita *et al.* 1999). The kinetics of the adsorption of metal and uranyl ions onto amidoximated *Pinus densiflora* bark was studied by Mun *et al.* (2010). To the best of our knowledge, there are no reports on the application of this biosorption study for the removal of phenolic compounds from aqueous solutions. The aim of the present work is to study the removal of phenolic compounds by pine bark material from synthetic wastewater and to offer this biosorbent as a local substitute for existing commercial adsorbent material.

Therefore, the main objective of this present research work is to investigate the biosorption potentiality of pine bark biosorbent material for the removal of phenol, 2-chlorophenol (2-CPh), and 4-chlorophenol (4-CPh) from aqueous medium. Further, the biosorbent was characterized by Brunauer-Emmett-Teller (BET) surface area, Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), X-ray diffractometer (XRD), and elemental analysis for carbon, hydrogen, and nitrogen (CHN) to identify the functional groups, crystallinity and surface morphology, and elemental mapping. The effects of factors such as contact time, biosorbent dosage, pH, and initial adsorbate concentrations on this biosorption process were investigated using a batch equilibrium technique.

MATERIALS AND METHODS

Materials

Pine bark (*Pinus densiflora* Sieb.) was collected from the campus woods at Dongguk University, Gyeongju, South Korea, in June, 2011, for the preparation of biosorbent. The 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 50, 100, 150, and 200 mg/L solutions of phenol, 2-CPh, and 4-CPh. To adjust pH, 0.1 M HCl and 0.1 M NaOH were obtained from Samchun Chemicals, South Korea. Water used for the preparation of solutions and cleaning adsorbents was generated in the laboratory by double distilling deionized water in a quartz distillation unit.

Characterization

X-ray diffraction (XRD) measurements were carried out using a D5000 (Siemens; Germany) diffractometer equipped with a copper anode ($\text{Cu K}\alpha = 1.5406 \text{ \AA}$) over a scanning interval (2θ) value ranging from 10 to 50°. Elemental (CHN) analyses were recorded using a Thermo Finnigan Flash EA 1112 CHN analyzer (Thermo Fisher Scientific, USA) for the pine bark powder biosorbent. The BET surface area of the pine bark powder was determined on a QUADRASORB analyzer (Quantachrome Instruments; USA) by nitrogen adsorption at -196 °C. Fourier transform infrared spectra of pine bark

powder, in virgin form and loaded with phenolic compounds, were obtained using a Nicolet-740, Perkin-Elmer model 283B (USA). The sample was prepared as a KBr pellet by investigating the peaks within the range 4000–400 cm⁻¹. A variable pressure SEM (Model Evo MA 15; Carl Zeiss; England) was used to characterize the surface morphology of the pine bark powder. The sample was analyzed using the back-scattered electrons, and images were then obtained at 800x and 1000x magnification with an accelerating voltage of 10.0 kV.

Preparation of Biosorbent

The local pine tree bark was first washed with distilled water to remove mud and dirt and then dried for 48 h in an oven at 60 °C. Then, the bark material was ground into a very fine particle size. The fine pine bark was soaked in 0.1 M NaOH to remove lignin materials, followed by soaking in 0.1 M H₂SO₄. Finally, it was washed with distilled water several times and dried in an oven at 70 to 80 °C for 6 to 9 h and cooled at room temperature in desiccators. The dried pine bark powder was stored in desiccators until used. The dried bark was sieved to 55- to 75-µm mesh with a standard testing sieve and used as a biosorbent for phenolic compound adsorption.

Batch Adsorption Studies

To optimize the adsorption of phenolic compounds, the effect of experimental conditions such as pH, contact time, biosorbent dosage, and initial adsorbate concentration were studied. In adsorption equilibrium, experiments were conducted in a set of 125-mL Erlenmeyer flasks, where 100-mL solutions of phenolic compounds (phenol, 2-CPh, and 4-CPh) with different initial concentrations (50 to 200 mg/L) were added to these flasks. The initial pH of the solution was adjusted using 0.1 M HCl/NaOH solution. Pine bark powder (0.1 g) was added to the phenolic compound solutions, and each sample was kept in a shaking water bath at 30 ± 1 °C and 220 rpm for 120 min to reach equilibrium. Samples were taken from the tubes, and the solutions were separated from the adsorbent by filtering through Whatman No. 50 filter paper (2.7 µm particle retention) to eliminate any fine particles. Then, the concentration of phenolic compounds was determined by measuring absorbance using a 1601 UV/Vis spectrophotometer (Shimadzu; 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) was calculated from the following equation:

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

where C_0 and C_{eq} (mg/L) are the initial and equilibrium liquid-phase concentrations of the phenolic compounds, respectively. V (L) is the volume of the solution, and m is the mass (g) of the dry pine bark powder used. For batch kinetic studies, the same procedure was followed, but the aqueous samples were taken at preset time intervals. The concentrations of phenolic compounds were similarly measured. The amount of uptake at time t , q_t (mg g⁻¹), was calculated as:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (2)$$

where C_t (mg/L) is the liquid-phase concentration of phenolic compounds at time t (min).

RESULTS AND DISCUSSION

Characterization of the Biosorbent

Fourier transform infra-red (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), elemental (CHN), and surface area by nitrogen adsorption (BET) analyses were carried out to characterize the pine bark powder. Physicochemical characterization of pine bark was performed to understand the mechanism involved in the biosorption process. The moisture content, bulk density, ash content, CHN, and surface properties (such as surface area and pore radius) are presented in Table 1.

Table 1. Physical, Surface Characterization, and Elemental Analysis of Pine Bark Powder Biosorbent

Parameter	Value
Color	Light Brownish
Odor	None
Weight loss (%)	42.6
Apparent (bulk) density (g/cm ³)	0.318
Moisture content (%)	5
Ash content (%)	5.62
BET surface area (m ² /g)	0.104
Multi point BET surface area (m ² /g)	1.410
Pore radius (Å ⁰)	22.35
Carbon (%)	76.41
Hydrogen (%)	5.35
Nitrogen (%)	6.78

FTIR Analysis

Characterization of the biosorbent was carried out by Fourier Transform Infrared Spectroscopy to determine the type of functional groups on the biosorbent. FTIR spectroscopy was used to obtain information on the nature of possible adsorbent-adsorbate interactions. FTIR spectra in the range of 4000 to 400 cm⁻¹ for the virgin pine bark powder and pine bark powder loaded with phenol, 2-CPh, and 4-CPh are shown in Fig. 1, profiles (a), (b), (c), and (d), respectively. The FTIR spectroscopic characteristics are shown in Table 2. The FTIR spectrum of pine bark powder before adsorption (Fig. 1a) shows a broad absorption peak at 3372 cm⁻¹ corresponding to the overlapping -OH and -NH peaks. A peak at 2921 cm⁻¹ represents the C-H group. The C=O stretching of pure pine bark powder was at 1617 cm⁻¹. The presence of -C-N linkages is confirmed from the peaks at 1058 cm⁻¹. As shown in Fig. 1b, c, and d, a significant difference can be seen in the FTIR spectra of biosorbent before and after biosorption. Some peaks were slightly shifted and/or broadened, indicating that the functional groups present on the biosorbent are involved in interaction with the phenolic compounds. These results confirm the participation of the amino, carboxyl, and hydroxyl groups of pine bark powder as potential active binding sites for the adsorption of phenol, 2-CPh, and 4-CPh.

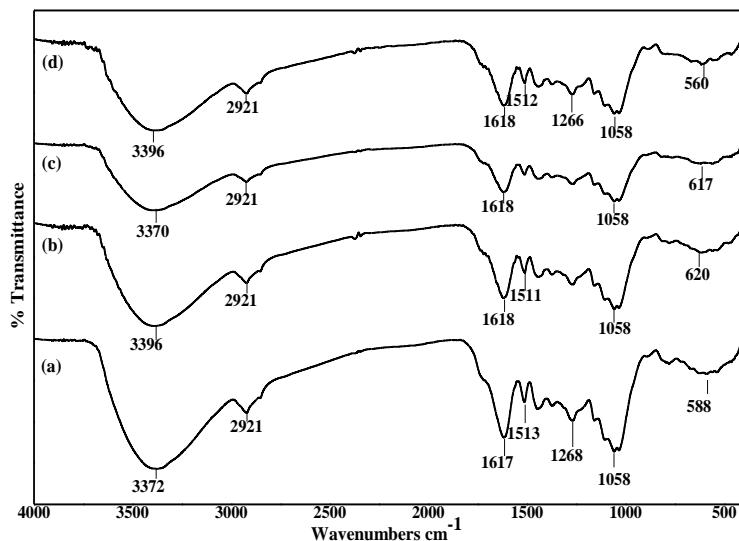


Fig. 1. FTIR spectra of pine bark powder: (a) before biosorption; (b) after phenol biosorption; (c) after 2-CPh biosorption; and (d) after 4-CPh biosorption

Table 2. Wave Number (cm^{-1}) for the Dominant Peak from FTIR for Phenolic Compounds Adsorption

Functional groups of pine bark powder	Virgin pine bark powder	Phenol loaded pine bark powder	2-CPh loaded pine bark powder	4-CPh loaded pine bark powder
Surface O-H stretching	3372	3396	3370	3396
Aliphatic C-H stretching	2921	2921	2921	2921
C=O stretching	1617	1618	1618	1618
Aromatic C-NO ₂ stretching	1513	1511	-	1512
-SO ₃ stretching	1268	-	-	1266
C-N aliphatic amines	1058	1058	1058	1058
Functional groups	588	620	617	560

XRD Analysis

An X-ray diffraction analysis was performed on virgin pine bark powder. The pine bark powder exhibited a broad peak at $2\theta = 29.8^\circ$ (figure not shown), indicating the amorphous state of the biosorbent.

Scanning Electron Microscope (SEM) Studies

The morphology of the pine bark powder consisted of a brick type, plate-like structure (Fig. 2a) with an agglomerated and irregular surface structure. The coarse surfaces of pine bark powder have an irregular structure, indicating that it has high porosity, thus making it possible for the adsorption of phenol, 2-CPh, and 4-CPh on different parts of the biosorbent (Fig. 2b).

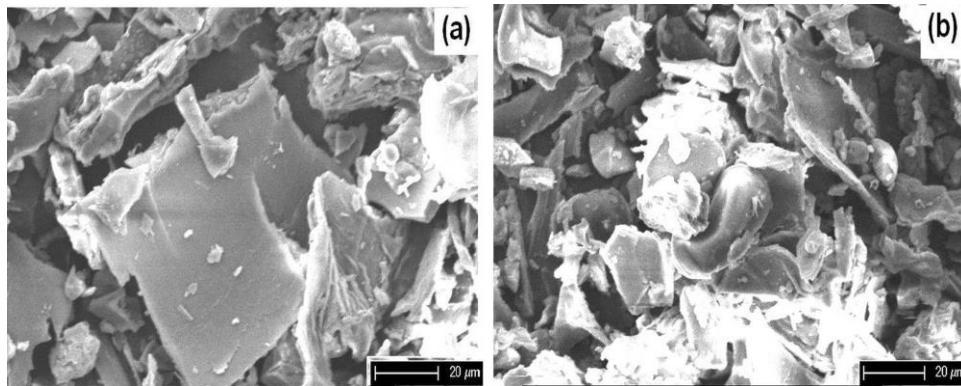


Fig. 2. Scanning electron micrographs of the pine bark powder at (a) 1000x and (b) 800x magnification

Effect of pH

The pH is the most important parameter affecting the degree of ionization and the allocation of various pollutants, leading to changes in the reaction kinetics and equilibrium characteristics of the sorption process. To optimize the pH to achieve maximum removal efficiency, experiments were conducted over a wide range of pH, from 2.0 to 10.0, using 0.1 g of pine bark with 100 mL of 100 mg/L adsorbate solutions at 30 ± 1 °C. In the alkaline range, the pH was varied using aqueous 0.1 M NaOH, whereas in the acidic range, the pH was varied using 0.1 M HCl. Experimental results indicate that phenol, 2-CPh, and 4-CPh were most effectively removed by pine bark at pH 6.0; the removal efficiency decreased on either side of these pH values (Fig. 3).

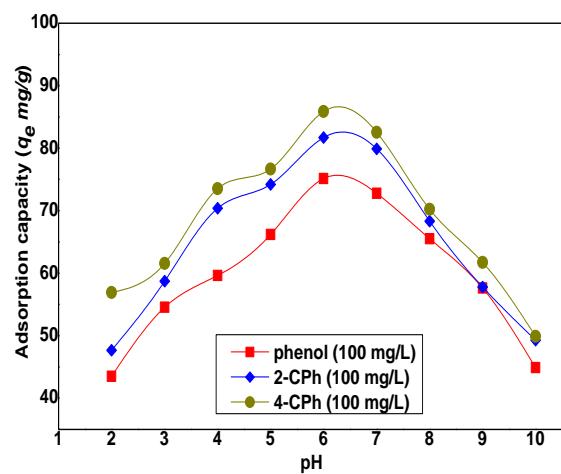


Fig. 3. Effect of pH on the biosorption of (■) phenol, (◆) 2-CPh, and (●) 4-CPh onto pine bark powder. Experimental conditions: initial concentrations = 100 mg/L, contact time = 3 h, biosorbent dosage = 0.1 g/0.1 L, temp = 30 ± 1 °C, and agitation rate = 220 rpm.

The effect of solution pH on the removal efficiency of phenol and its derivatives from aqueous solutions can be explained by considering the presence of ionic and molecular forms of phenolic compounds in aqueous solutions. The phenolic compounds considered in this study, *i.e.*, phenol, 2-CPh, and 4-CPh, have pKa values of 9.9, 8.3, and 9.2, respectively, suggesting that phenol is a weak acid; hence, they mostly exist as anions

at high pH values (Kumar and Min 2011a). When the pH of a solution surpasses the pK_a , phenols chiefly exist as negative phenolate ions, whereas they exist as neutral molecules below the pK_a . Because of the electron-rich nature of the oxygen atom in phenolate ions, the hydrogen bonding efficiency decreases. Therefore, phenols are effectively adsorbed on to the adsorbent as neutral molecules, not phenolate ions. From the experimental results, pH 6.0 was selected as the optimum pH value.

Effect of Biosorbent Dosage

The effect of different doses of pine bark on the removal of phenol, 2-CPh, and 4-CPh was determined, and the results are presented in Figs. 4a through 4c. The amount of adsorbent was varied from 0.05 to 0.8 g while variables such as pH, rpm, contact time, and temperature were kept constant.

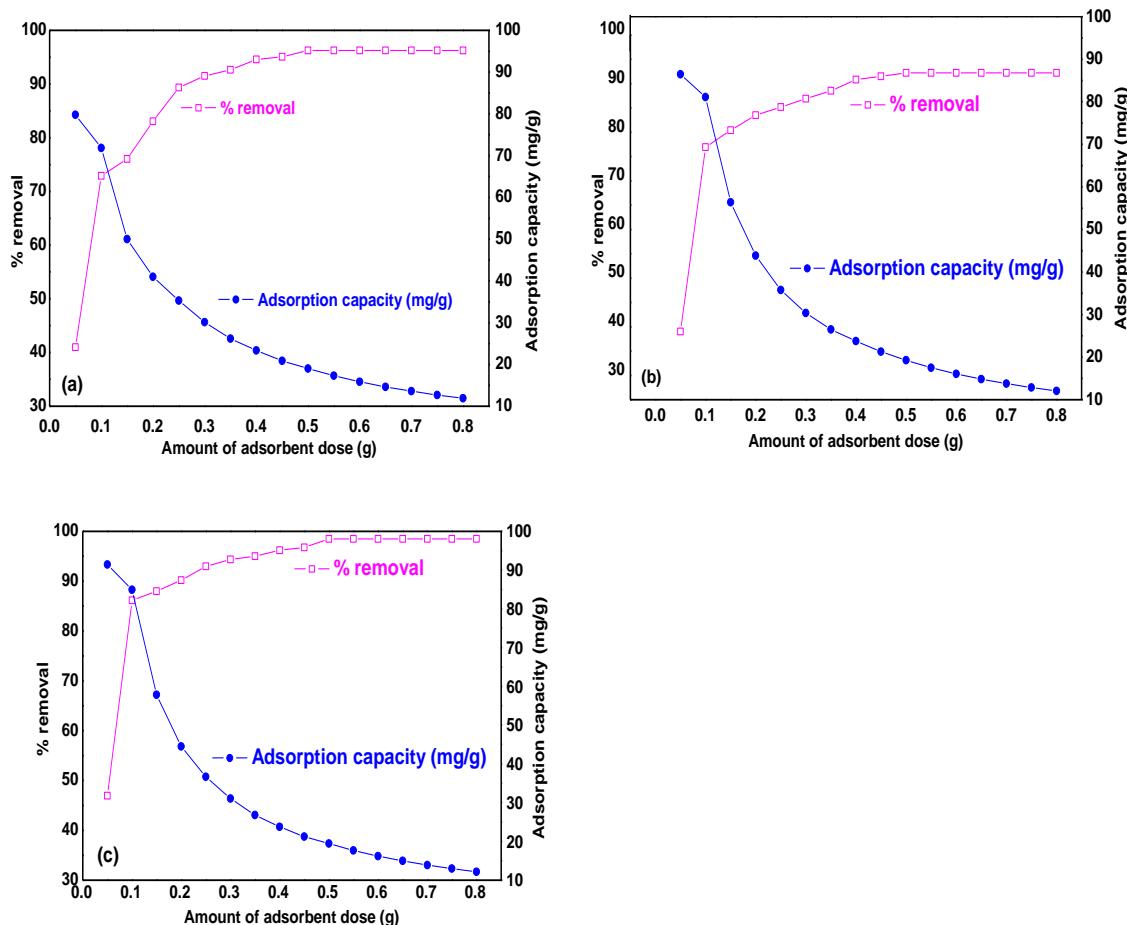


Fig. 4. Effect of biosorbent dosage on the biosorption of (a) phenol, (b) 2-CPh, and (c) 4-CPh onto pine bark powder [(% removal of phenol, 2-CPh, 4-CPh, and biosorption capacity (mg/g)]. Experimental conditions: initial concentration = 100 mg/L, biosorbent dosage = 0.05 to 0.8 g, contact time = 120 min, and pH = 6.0.

It can be seen from the figures that the percentage removal of phenol, 2-CPh, and 4-CPh increased with increasing adsorbent dose, while the loading capacity, q_e (mg/g), (amount of phenol, 2-CPh, and 4-CPh loaded per unit weight of adsorbent) gradually

decreased. This growth can be attributed to the additional number of adsorption sites, which resulted from the increase in the adsorbent dosage. The decrease in the total adsorbed amount of phenols (q_e) as the adsorbent dose increased can be attributed to the aggregation or overlap of the adsorption sites due to the overcrowding of adsorbent particles, which decreases the total adsorbent surface area available to the phenols. It can also be seen from Figs. 4a through 4c that the solute uptake markedly increased to an adsorbent dose of 0.5 g/0.1 L; thereafter, no significant increase was observed. The binding rate of phenolic compounds with adsorbent increases more rapidly in the initial stages; after a certain point, the adsorption is marginal and becomes almost constant.

Effect of Contact Time and Initial Concentration

Contact time and initial concentration have a pronounced effect on the removal of adsorbate species from aqueous solutions. The effect of agitation time on the extent of adsorption of phenolic compounds at different concentrations is shown in Figs. 5, 6, and 7 for phenol, 2-CPh, and 4-CPh, respectively.

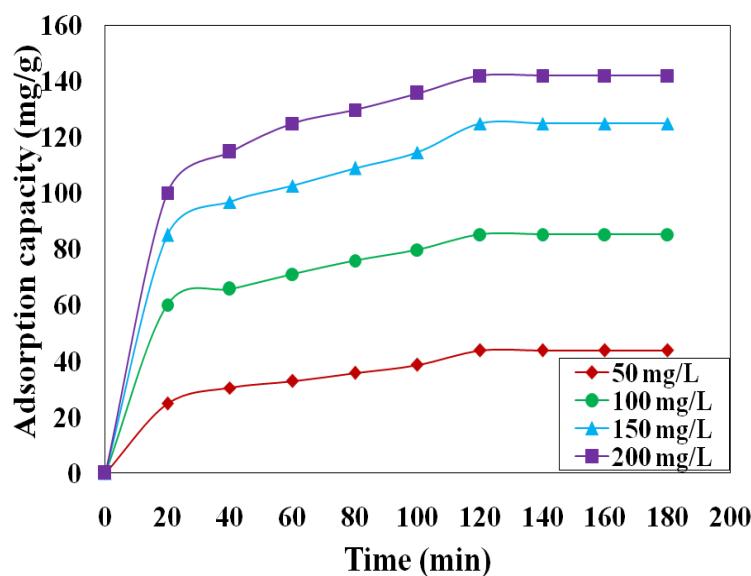


Fig. 5. Effect of contact time on phenol adsorption. Different initial phenol concentrations (◆) $C_0 = 50 \text{ mg/L}$, (●) $C_0 = 100 \text{ mg/L}$, (▲) $C_0 = 150 \text{ mg/L}$, (■) $C_0 = 200 \text{ mg/L}$; pH = 6.0; biosorbent dosage = 0.1 g/0.1 L; contact time = 120 min; agitation rate = 220 rpm; temp = $30 \pm 1^\circ\text{C}$

The effect of shaking time on the biosorption of phenolic compounds onto pine bark powder was studied over a range of 20 to 180 min, using 0.1 g/0.1 L of pine bark powder, 50 to 200 mg/L of phenolic compounds at pH 6.0, $30 \pm 1^\circ\text{C}$, and a shaking speed of 220 rpm. 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 50 to 200 mg/L to reach equilibrium was 120 min. 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 pine bark powder. Therefore, the optimum contact time was selected as 120 min for further experiments.

However, for adsorbate solutions with higher initial concentrations, lower equilibrium times were required. An increase in initial adsorbate 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.

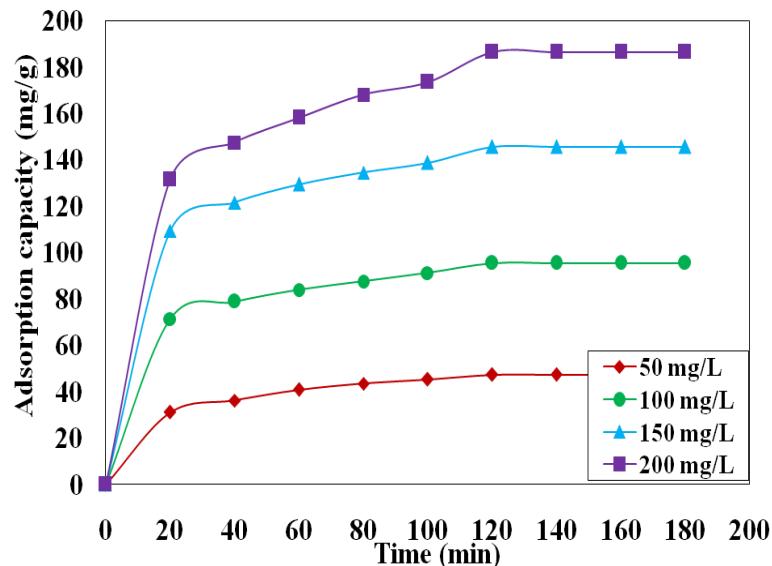


Fig. 6. Effect of contact time on 2-CPh adsorption. Different initial 2-CPh concentrations (◆) $C_0 = 50$ mg/L, (●) $C_0 = 100$ mg/L, (▲) $C_0 = 150$ mg/L, (■) $C_0 = 200$ mg/L; pH = 6.0; biosorbent dosage = 0.1 g/0.1 L; contact time = 120 min; agitation rate = 220 rpm; temp = 30 ± 1 °C

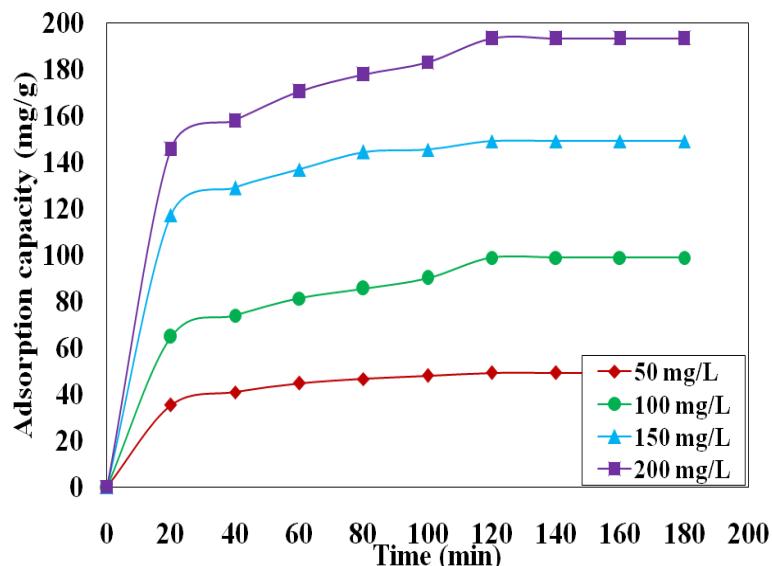


Fig. 7. Effect of contact time on 4-CPh adsorption. Different initial 4-CPh concentrations (◆) $C_0 = 50$ mg/L, (●) $C_0 = 100$ mg/L, (▲) $C_0 = 150$ mg/L, (■) $C_0 = 200$ mg/L; pH = 6.0; biosorbent dosage = 0.1g/0.1 L; contact time = 120 min; agitation rate = 220 rpm; temp = 30 ± 1 °C

KINETIC STUDIES

Several kinetic models (the model of diffusion on homogeneous surface, the model of the diffusional pores, the heterogeneous model of diffusion, and the model of Elovich) were tested on our experimental results to describe the mechanism of the process of adsorption (mass transfer, chemical reaction). Four kinetic models, pseudo-first order, pseudo-second order, Elovich, and the intraparticle diffusion model, were considered to investigate the behavior of the adsorption process of phenolic compounds onto pine bark.

The pseudo-first-order kinetic model was suggested by Lagergren and is widely used for the description the sorption of liquid on solid (Lagergren 1898). The linear form of the pseudo-first-order rate equation is generally expressed as follows,

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

where q_e (mg/g) and q_t (mg/g) are the amounts of adsorbate sorbed at equilibrium and at time t (min). k_1 is the rate constant of the first-order adsorption process. The pseudo-first order kinetic constants were determined from slope of the plot of $\log(q_e - q_t)$ versus t (figure not shown), and the values are shown in Table 2.

The kinetic data were further analyzed using Ho's pseudo-second-order kinetic model (Ho *et al.* 1999). The linearized form of the equation is expressed as:

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

The values of q_e and k_2 can be estimated experimentally from the slope and intercept of the plot of t/q_t versus t (figure not shown) and are given in Table 2. Adsorption of phenol, 2-CPh, and 4-CPh on pine bark satisfactorily followed the pseudo-second order rate equation. This was reflected by the high R^2 values (> 0.993) and the agreement between both the calculated and the experimental q_e values (Table 3).

To quantitatively compare the applicability of each model, a normalized standard deviation Δq_t (%) was calculated, defined as,

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

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_t (%), the better fit the model is for the data. The calculated rate constants for the models, their corresponding regression (R^2), and normalized standard deviation values are listed in Table 3. The results suggest that the higher R^2 values obtained with the pseudo-second-order kinetic model, lower Δq_t (%) values, and the calculated q_e (cal) values are closer to the experimental data than the calculated values of pseudo-first order kinetic model. From this observation it may be concluded that the adsorption of phenol, 2-CPh, and 4-CPh compounds on the pine bark powder follows pseudo-second order kinetics.

Table 3. Biosorption Rate Constants of Phenol, 2-CPh, and 4-CPh on Pine Bark Powder

Pseudo-first-order kinetic model					Pseudo-second-order kinetic model				
Phenol									
(mg/L)	q_e , exp (mg/g)	k_1 (min ⁻¹)	q_e , cal (mg/g)	R^2	Δq_t (%)	q_e , cal (mg/g)	k_2 (g/mg/min)	R^2	Δq_t (%)
50	43.84	0.013	26.12	0.985	4.0843	45.24	1.186×10^{-3}	0.993	0.0337
100	85.23	0.018	40.17	0.978	6.9877	90.90	9.168×10^{-4}	0.995	0.1106
150	124.95	0.016	55.71	0.989	7.6768	125.00	7.272×10^{-4}	0.997	4×10^{-6}
200	142.01	0.023	68.23	0.989	6.7480	166.66	4.931×10^{-4}	0.998	0.7532
2-CPh									
50	47.22	0.025	30.13	0.989	3.2747	52.63	1.222×10^{-3}	0.997	0.3281
100	95.35	0.020	38.99	0.984	8.7345	95.23	1.121×10^{-3}	0.998	3.96×10^{-5}
150	145.52	0.020	55.33	0.998	9.6030	153.84	7.545×10^{-4}	0.999	0.0817
200	186.51	0.016	80.35	0.997	8.0994	192.30	4.916×10^{-4}	0.998	0.0240
4-CPh									
50	49.18	0.027	36.24	0.997	1.7307	55.55	1.580×10^{-3}	0.999	0.4194
100	98.75	0.016	48.19	0.996	6.5536	100.00	7.874×10^{-4}	0.997	0.0040
150	149.11	0.027	59.97	0.975	8.9345	156.25	8.533×10^{-4}	0.999	0.3463
200	193.42	0.018	93.11	0.997	6.7239	196.07	6.049×10^{-4}	0.998	0.0289

Elovich Equation

The Elovich equation was first used in the kinetics of adsorption of gases on solids; it has been successfully applied for the adsorption of solutes from a liquid solution. The linear form of the Elovich equation is given as follows (Bulut *et al.* 2008):

$$q_t = \left(\frac{1}{b} \right) \ln(ab) + \frac{1}{b} \ln t \quad (7)$$

where a (mg/g min) is the initial sorption rate and the parameter b (g/mg) is a constant related to the extent of surface coverage and activation energy for chemisorptions. The parameters $(1/b)$ and $(1/b)\ln(ab)$ can be obtained from the slope and intercept of the linear plot of q_t versus $\ln t$. The plots are linear, with good correlation coefficient values (Table 4). The calculated q_e values from the Elovich model agreed quite well with the experimental equilibrium concentration values. This suggests that the sorption system studied belongs to the pseudo-second order kinetic model, based on the assumption that the rate-determining step may be chemisorption, involving valence forces through sharing or exchange of electrons between the adsorbent and adsorbate.

Intraparticle Diffusion Study

In diffusion studies, the rate can be expressed in terms of the square root of time. The mathematical dependence of Q_t versus $t^{1/2}$ is obtained if the process is considered to be influenced by diffusion in the particles and convective diffusion in the solution. According to the intraparticle diffusion model proposed by Weber and Morris (1963), the root time dependence may be expressed by the following equation:

$$Q_t = k_{id} t^{1/2} + C \quad (8)$$

where Q_t is the amount of solute on the surface of the sorbent at time t (mg/g), k_{id} is the intraparticle diffusion rate constant (mg/g min^{1/2}), and C is the intercept (mg/g); this gives an idea of the thickness of the boundary layer.

The k_{id} values are found from the slopes of Q_t versus $t^{1/2}$ plots and are shown in Figs. 8a through 8c. If the intraparticle diffusion is involved in the adsorption process, then the plot of the square root of time versus the uptake (Q_t) would result in a linear relationship, and the intraparticle diffusion would be the controlling step if this line passed through the origin.

When the plots do not pass through the origin, this is indicative of some degree of boundary layer control, which further shows that the intraparticle diffusion is not the only rate controlling step; other processes may control the rate of adsorption. From Table 4, it can be seen that the thickness of the boundary layer increased with increasing concentration.

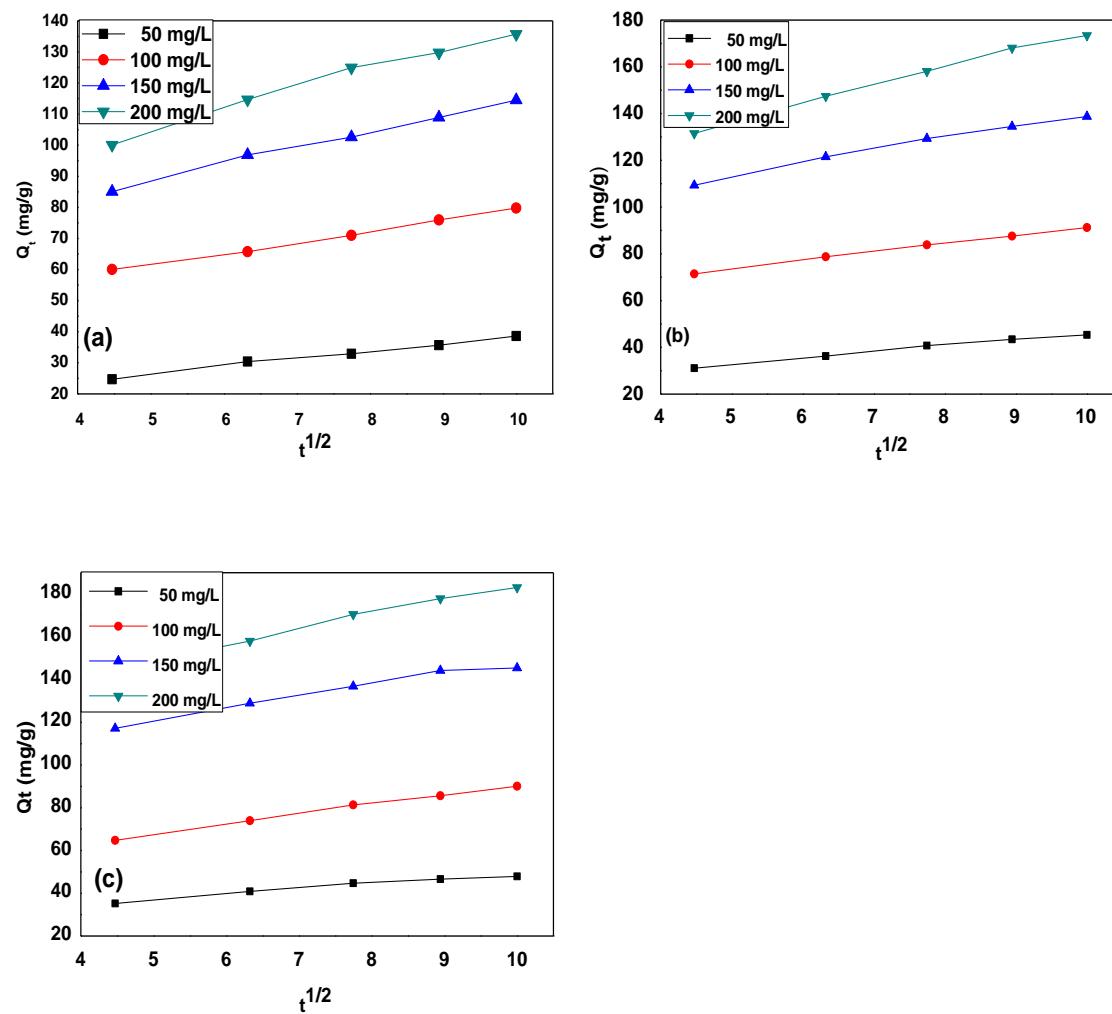


Fig. 8. Weber–Morris model plots for biosorption of (a) phenol, (b) 2-CPh, and (c) 4-CPh onto pine bark powder

Table 4. Biosorption Rate Constants of Phenol, 2-CPh, and 4-CPh on Pine Bark Powder

Elovich kinetic model					Intraparticle diffusion model				
Phenol									
(mg/L)	q_e , exp (mg/g)	q_e , cal (mg/g)	(1/b)ln(ab) (mg/g)	1/b (mg/g)	R ²	Δq_t (%)	k_{id}	C	R ²
50	43.84	54.74	8.32	9.69	0.938	1.2363	2.721	12.38	0.973
100	85.23	82.41	17.16	13.63	0.958	0.0218	3.609	43.45	0.997
150	124.95	119.71	21.57	20.50	0.949	0.0351	5.210	62.52	0.994
200	142.01	132.24	31.00	22.85	0.995	0.0946	6.397	73.09	0.985
2-CPh									
50	47.22	52.84	3.29	9.132	0.996	0.2833	2.631	19.62	0.992
100	95.35	93.72	31.4	13.02	0.985	0.0058	3.568	55.81	0.997
150	145.52	143.30	50.24	19.44	0.990	0.0046	5.323	86.78	0.989
200	186.51	181.03	41.63	29.12	0.971	0.0172	7.690	98.04	0.995
4-CPh									
50	49.18	49.51	11.96	7.84	0.995	0.0009	2.313	25.70	0.971
100	98.75	102.72	9.77	17.75	0.960	0.0323	4.584	44.80	0.995
150	149.11	149.54	62.65	18.15	0.992	0.0001	5.331	94.57	0.976
200	193.42	189.73	65.62	25.85	0.975	0.0087	6.953	114.9	0.992

EQUILIBRIUM ADSORPTION ISOTHERM MODELS

The capacity of the adsorption isotherm is fundamental and plays an important role in the determination of the maximum adsorption capacity. Three isotherm equations have been tested in the present study to analyze the equilibrium data of the adsorbent: Langmuir, Freundlich, and Dubinin-Radushkevich. Analysis of the adsorption equilibrium data was done on the widely used Langmuir and Freundlich adsorption isotherms equations, which provide information on the relationship between the quantity of adsorbate removed and the concentration of the adsorbate remaining in the liquid phase at equilibrium.

The Langmuir theory was first used to describe the adsorption of gas molecules on solid surfaces. However, it has since been successfully applied to mass transfer processes from liquid to solid phase for describing the mechanism of adsorption. Theoretically, it depicts a monolayer uptake of the adsorbate on a homogenous adsorbent surface having uniform binding energy at all binding sites. The Langmuir (Kumar and Min 2011a) adsorption equation is expressed as:

$$\frac{1}{q_e} = \frac{1}{Q^0} + \left(\frac{1}{bQ^0} \right) C_e \quad (9)$$

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, and Q^0 and b are Langmuir constants related to the adsorption capacity and rate of adsorption, respectively. The linear plot of $1/C_e$ versus $1/q_e$ indicates that adsorption obeys the Langmuir model.

The Langmuir parameters can be further used to predict the affinity between the adsorbate and adsorbent using the dimensionless separation factor (R_L) (Kumar and Min 2011b) as follows,

$$R_L = \frac{1}{1+bC_0} \quad (10)$$

where R_L is the dimensionless separation factor, C_0 is the initial concentration of the adsorbate (mg/L), and b is the Langmuir constant (L/mg). The R_L parameter is considered a more reliable indicator of the adsorption. The R_L value predicts the fate of the adsorption system, as favorable ($0 > R_L > 1$), unfavorable ($R_L < 1$), linear ($R_L = 1$), or irreversible ($R_L = 0$). The value of R_L is less than 1 and greater than 0, suggesting the favorable uptake of phenol, 2-CPh, and 4-CPh compounds by pine bark powder.

The Freundlich isotherm model (Kumar *et al.* 2012) is an empirical description based on the adsorption on a heterogeneous surface containing binding sites having different energies, represented as,

$$q_e = K_F C_e^{1/n} \quad (11)$$

where K_F ((mg/g)(L/mg)^{1/n}) and (1/n) are Freundlich constants that indicate relative adsorption capacity and adsorption intensity, respectively, and $n > 1$ indicates favorable adsorption. The linear form of Eq. 9 is,

$$\ln q_e = \ln K_F + \left(\frac{1}{n} \right) \ln C_e \quad (12)$$

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 $\ln(C_e)$.

The Dubinin-Radushkevich (1947) isotherm was used to fit with experimental data, and it can be represented as,

$$q_e = q_s \exp(-B\varepsilon^2) \quad (13)$$

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

$$\varepsilon = RT \ln \left[1 + \frac{1}{C_e} \right] \quad (14)$$

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 using the relationship:

$$E = \frac{1}{\sqrt{2B}} \quad (15)$$

A plot of $\ln(q_e)$ versus ε^2 enables the constants q_s and E to be determined. E gives information about the nature of adsorption mechanism, whether it is a chemical ion exchange or a physical adsorption. If $8 < E < 16$ kJ/mol, then the adsorption process is a chemical ion-exchange process. If $E < 8$ kJ/mol, then the adsorption process is physical in

nature. Correlation coefficients and parameter values for the three isotherms were presented in Table 5. Based on the correlation coefficients, the applicability of the isotherms was compared. For all cases, the Langmuir equation fits the experimental data better than the Freundlich and Dubinin-Radushkevich equation. All the evaluated equilibrium models had a good fit with the experimental data, and it can be concluded that the Langmuir is the best model describing adsorption of phenolic compounds on the pine 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 6 along with the values obtained in the present study.

Table 5. Isotherm Parameters of Langmuir, Freundlich, and D-R Isotherms for Adsorption of Phenol, 2-CPh, and 4-CPh on Pine Bark Powder

Adsorbates	Langmuir constants			Freundlich constants			Dubinin-Radushkevich Isotherm			
	Q_0 (mg/g)	b (L/mg)	R^2	K_F ((mg/g) (L/mg) $^{1/n}$)	n	R^2	B	q_s (mg/g)	E (kJ/mol)	R^2
Phenol	142.85	0.029	0.994	4.130	1.166	0.978	0.004	4.594	11.18	0.801
2-CPh	204.08	0.030	0.996	6.295	1.200	0.998	0.003	4.825	12.90	0.917
4-CPh	263.15	0.021	0.995	5.357	1.076	0.987	0.002	3.412	13.86	0.810

Table 6. Maximum Adsorption Capacities, Q_0 (mg/g), for the Adsorption of Phenol, 2-CPh and 4-CPh Compounds by Various Adsorbents

Adsorbates, Q_0 (mg/g)				
Sorbent	Phenol	2-CPh	4-CPh	References
Brown alga <i>Sargassum muticum</i>	4.6	79.0	251.0	Rubin <i>et al.</i> (2006)
<i>Pleurotus sajor-caju</i> fungus	89.3	159.4	188.9	Denizli <i>et al.</i> (2005)
<i>Phanerochaete chrysosporium</i> fungus	115.7	191.5	228.8	Denizli <i>et al.</i> (2004)
CS/CA blended beads	109	97	-	Siva Kumar <i>et al.</i> (2008)
<i>Trametes versicolor polyporus</i> fungus	50	86	112	Kumar <i>et al.</i> (2009)
<i>A. leucocephala</i> bark powder	94.33	147.05	181.81	Kumar and Min (2011b)
CS/Ab blended beads	156	204	278	Kumar <i>et al.</i> (2009a)
chitosan-coated perlite bead	192	263	322	Kumar <i>et al.</i> (2010)
<i>Schizophyllum commune</i> fungus	120	178	244	Kumar and Min (2011a)
Pine bark Powder	142.85	204.08	263.15	Present study

CONCLUSIONS

1. Lignocellulosic agriculture waste, *i.e.*, pine bark powder, was utilized as a biosorbent for the removal of phenolic compounds (phenol, 2-CPh, and 4-CPh) from aqueous environments.
2. The biosorbent was characterized by FTIR, XRD, BET, CHN analyzer, and SEM techniques.

3. The adsorption rate process was fast, reaching equilibrium in a short time (almost 120 min).
4. When the pine bark biosorbent dosage was increased, the equilibrium adsorption capacity (mg/g) of pine bark gradually decreased, whereas the percent removal efficiency increased.
5. The good correlation coefficients and the agreement between experimental and calculated values of q_e and lower Δq_t (%) values showed that the phenolic compounds adsorption followed pseudo-second order kinetics.
6. The experimentally determined Q_{0max} of pine bark powder for phenol, 2-CPh, and 4-CPh was 142.85, 204.08, and 263.15 mg/g, respectively, which agree well with the predicted Langmuir Q_{0max} values. The experimental equilibrium data could be well interpreted by the Langmuir isotherm. The adsorption of phenolic compounds was rated as favorable, based on R_L values.
7. Considering the present findings, it can be concluded that pine bark powder, an abundantly and locally available low-cost biosorbent, has a considerable adsorption capacity with the potential for use as an alternative sorbent for the removal of phenol, 2-CPh, and 4-CPh compounds from aqueous media.

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