Water polishing of phenol by walnut green hull as adsorbent: an insight of adsorption isotherm and kinetic

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ABSTRACT

The present paper aims to investigate water purification of phenol by walnut green hull adsorbent. The surface characteristics of the adsorbent were studied using Fourier transform infra-red (FTIR), scanning electron microscope, and X-ray diffraction (XRD) techniques. The presence of functional groups such as hydroxyl and carbonyl onto walnut green hull surface was proved by FTIR analysis. Also quartz, cellulose and hematite were detected in the XRD analysis of samples by an X-ray diffractometer. The maximum sorption was achieved at pH 4.0. Data were evaluated for compliance with the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm models. The results indicate that the data for adsorption of phenol onto walnut green hull fitted well with the Langmuir isotherm. The maximum adsorption capacity of the adsorbent was achieved by Langmuir isotherm 17.8 mg g^{-1}. Also, the adsorption kinetics of phenol on the adsorbent were studied. The rates of sorption were found to conform to pseudo-second-order kinetics with good correlation.

Key words | isotherm, kinetic, phenol, walnut green hull, wastewater

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INTRODUCTION

Phenol compounds are harmful to plants, animals and humans, even at low concentrations. They are among the most prevalent forms of organic chemical pollutants in industrial wastewaters (Busca *et al.* 2008). Phenol compounds are released into the environment as a result of pesticides and dye manufacturing industries such as paper and pulp, resin manufacturing, gas and coke manufacturing, tanning, textile, plastic, rubber, pharmaceuticals, and petroleum (Kurniawan

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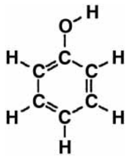
et al. 2010; Ghosh *et al.* 2012). Phenol and its derivatives have been designated as priority pollutants and are a probable human carcinogen since they are harmful for organisms at low concentrations and many of them have been classified as hazardous pollutants (Bilgili *et al.* 2012; Mustafa & Shihab 2013). The chemical and physical properties of phenol are summarized in Table 1. They have been found worldwide in water supplies, soil and air samples, food products and human tissue. In the presence of chlorine in drinking water, phenols form chlorophenol, which causes an unpleasant taste and odor in drinking water (Manojlovic *et al.* 2007). Their presence in the effluent of sewage treatment plants indicates their resistance to conventional chemical and biological treatments. Due to the stability of the phenol, its recalcitrant nature, slow degradation and not being amenable to biodegradation, it is difficult to remove from the environment by conventional treatment technologies (such as biological treatment) (Manojlovic *et al.* 2007; Catrinescu *et al.* 2011). The threshold value of phenol in water is 4,000 μg L^{-1}. Therefore it is important to use an effective and economic method to eliminate phenol from wastewater before discharging into any water body (Ahmaruzzaman 2008). There are many methods to remove phenol from wastewater. The adsorption process is one of the well-established and powerful techniques to remove organic compounds from wastewater. Mechanisms of the adsorption process include electrostatic forces, ion change, dipole-dipole interactions, covalent bonding and water bridging (Pigatto *et al.* 2013). In the present study, walnut green hull as an adsorbent prepared from agricultural wastes is considered to be an effective method for the removal of phenol from water solutions because of its large surface area, micro-porous nature, high adsorption capacity, high purity and easy availability. Also it has a porous structure consisting of a network of interconnected macropores, mesopores and micropores that provide good capacity for the adsorption of organic compounds from water solutions. The walnut green hull has no significant commercial and industrial use, and contributes to a reduction of serious environmental problems (Sprynskyy *et al.* 2009; Moussavi & Barikbin 2010; Girish & Murty 2012).

Table 1 | Physical and chemical properties of phenol

Formula	C_6H_6O
Mol. mass	94.11 g mol^{-1}
Appearance	Transparent crystalline solid
Odor	Sweet and tarry
Density	1.07 g cm^{-3}
Molecular structure	
Alternative name	Carbolic acid, phenilic acid, phenic acid
Melting point	40.5 °C (104.9 °F; 313.6 K)
Boiling point	181.7 °C (359.1 °F; 454.8 K)
Solubility in water	8.3 g/10 mL (20 °C)
Acidity (pK_a)	9.95 (in water), 29.1 (in acetonitrile)

MATERIALS AND METHODS

Preparation of adsorbent

Walnut green hull was obtained from a food factory and was dried in an air oven at 65 °C for a period of 48 h. Walnut green hull was soaked in acetone solution to remove green dye for 48 h. It was washed several times with distilled water to remove surface impurities. To increase the active surface of the adsorbent, it was mixed with 1% HCl for 24 h. Materials were then filtered, washed with distilled water, dried in an oven at 75 °C for a period of 24 h and sieved before use.

Adsorbent characterization

A scanning electron microscope (SEM) (Jeol Model Jsm-T330) was applied to study the morphological details of the adsorbent. It was used to observe the walnut green hull before and after adsorption by ESEM-FEG/GSED-Philips. Infrared spectra (Perkin-Elmer 1600 series Fourier transform infra-red (FTIR)) of adsorbent samples were measured in a wavenumber range between 400 and 4,000 cm^{-1} via powdered samples that encapsulated with KBr to prepare translucent sample disks. The powder X-ray diffraction (XRD) technique using Panalytical 3040/60 X‘ Pert PRO with a Cu Kα radiation source over a range of 10–120 at a scan speed of 1 s/step, 1.54 Å wavelength and 25 °C was used to measure adsorbent compound formation.

Zeta potential measurement

The zero point of charge for adsorbent was determined to investigate the change of surface charge of the adsorbent material at different pH levels. To determine pH_{zpc}, 50 mL of potassium nitrate (0.01 M) solution was added to Erlenmeyer flasks. The initial pH solution was adjusted between 2 and 12 by the addition of HCl and NaOH. Then 0.2 g of adsorbent was added to the Erlenmeyer flasks and mixed for 24 h. The final pH of the solution was measured using a pH meter (model 50-pp-sartorious). The curve of initial pH versus final pH was plotted and the intersection point of the curves was recorded as pH_{ZPC}.

Adsorption studies

Batch experiments were carried out in a cylindrical glass reactor (containing a volume of 10 mL in each case) with a magnetic stirrer using a constant speed of 120 rpm. Desired concentrations of phenol were obtained by diluting the stock solution. To study the pH, 0.1 g of adsorbent and 10 mL of phenol solution (10 mg L^{-1}) with a range of pH values from 3 to 10 were transferred into a conical flask, and flasks were agitated on a shaker at 120 rpm for 48 h, the time required for equilibrium. The pH of the solution was adjusted with either 0.1 N HCl or 0.1 N NaOH using a pH meter. Adsorption isotherm experiments were carried out in glass beakers at room temperature on a reciprocating shaker (120 rpm) for 72 h to reach adsorption equilibrium. The walnut green hull, with a constant mass of 0.1 g, was mixed with phenol samples with different concentrations of 10–70 mg L^{-1}. After completing the test, samples were collected from the supernatant and were analyzed for residual pollutant concentration. The kinetics of adsorption were investigated by shaking 0.1 g of adsorbent with different concentrations of pollutant in contact times from 3–60 min using a reciprocating shaker at a speed of 120 rpm. Finally, the residual concentration of pollutant in the supernatant was analyzed. All experiments were carried out according to Standard Methods. After each step, the adsorbent was separated from the reaction mixture by centrifugation at 3,000 rpm for 3 min. The phenol residual amount was determined by the 5530 D method, mentioned in the Standard Method, at 500 nm, using a spectrophotometer (Gernjak *et al.* 2006). Each experiment was conducted three times.

RESULTS AND DISCUSSION

The SEM micrographs are very useful in obtaining the adsorption details of the walnut green hull adsorbent. SEM images are shown in Figure 1. The physical properties and surface morphology of the adsorbent indicated that the walnut green hull adsorbent has more micropore structures and higher surface area. So, it has a high adsorption capacity, due to the raw material of walnut green hull having more cellulose content. Comparing the images of before (Figure 1(a)) and after (Figure 1(b)) the adsorption process, it was observed

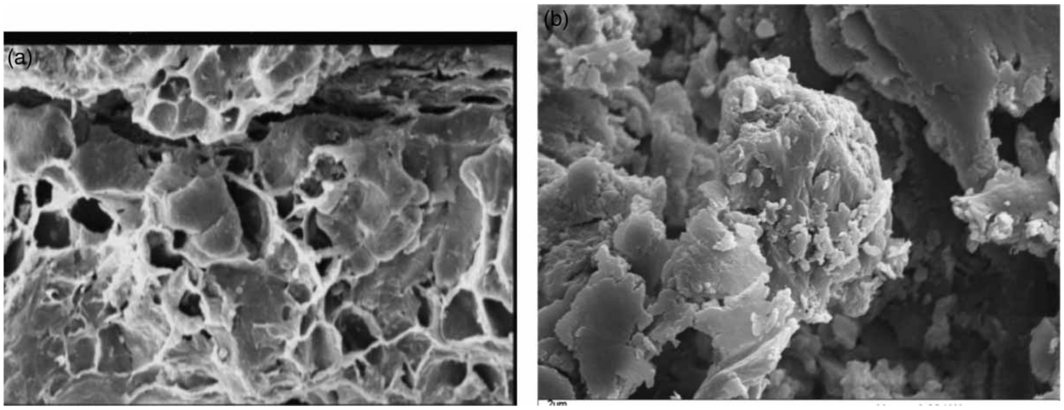


Figure 1 | SEM images of the walnut green hull adsorbent before (a) and after phenol adsorption (b).

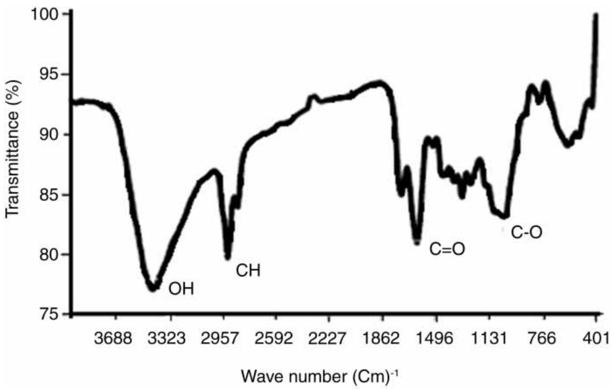


Figure 2 | Infrared spectrum of walnut green hull.

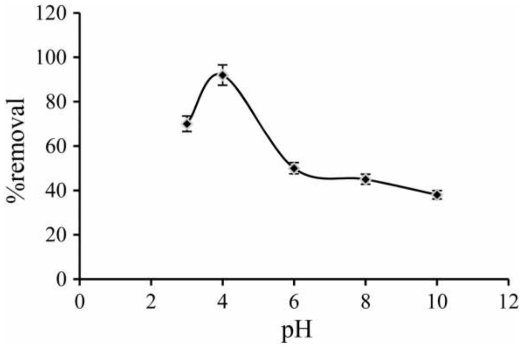


Figure 4 | Effect of the solution pH in the adsorption of phenol onto walnut green hull ($C_0 = 10$ mg L^{-1}, adsorbent dose = 1 g L^{-1}, $t = 48$ h and $T = 25 \pm 1$).

that after phenol removal from solution, the surface of the adsorbent was completely covered with phenol.

The FTIR spectra of the walnut green hull adsorbent were used to determine the positions of different bands, their assignments and the functional groups in the adsorbent. Figure 2 exhibits IR spectrums of walnut green hull adsorbent. As shown in Figure 2, the broad band at 3,323 cm^{-1} is due to the OH stretch group. The peaks of 110–800 cm^{-1} are attributable to the presence of C-O stretching vibration in carboxylic acids and alcohols. The peaks of 2,600–2,700 cm^{-1} are due to the contribution from C-H stretching. The absorption band at 1,526 cm^{-1} can be attributed to the carbonyl [C = O] stretching group.

The results of XRD analysis of the walnut green hull adsorbent are displayed in Figure 3. Quartz, cellulose and hematite were detected in the XRD analysis of samples by an X-ray diffractometer (Philips X'Pert Pro).

The pH plays an important role in the adsorption process due to its influence on the surface charge of adsorbent and ionization/dissociation of the adsorbate molecule. To survey the effect of pH on the removal efficiency of phenol, the pH was changed from 3 to 10 at an initial phenol concentration of 10 mg L^{-1} and adsorbent dose of 0.1 g per 10 mL of solution. The maximum removal efficiency of walnut green hull was observed at pH 4.0 (Figure 4). On considering the pH_{zpc} ($pH_{\text{zero point charge}}$) of walnut green hull ($pH_{zpc} = 4.9$) and the speciation of phenol at a pH of below 4.9, the surface of the walnut green hull is positively charged and favorable to the adsorption of phenol. At a pH of below 4.9, phenol will interact electrostatically with the positively charged surface of the sorbent. With increasing pH levels higher than the isoelectric point of the adsorbent, negatively charged sites on the surface of the walnut green adsorbent increased, which resulted in an electrostatic repulsion force between negatively charged phenol molecules and negatively charged sites on the surface of the adsorbent (Kim *et al.* 2004; Aguilar *et al.* 2005). Also, the low removal efficiency at high pH is due to the presence of phenolate ions that are attributed to phenol ionization [φ_{ions}]. At a high pH value, (φ_{ions} increase as the pH value increases), the presence of hydroxyl ions on the adsorbent prevents the uptake of phenolate ions (Smith & March 2007). Phenol is weakly acidic, and at high pHs gives the phenolate anion $C_6H_5O^-$ (also called phenoxide):

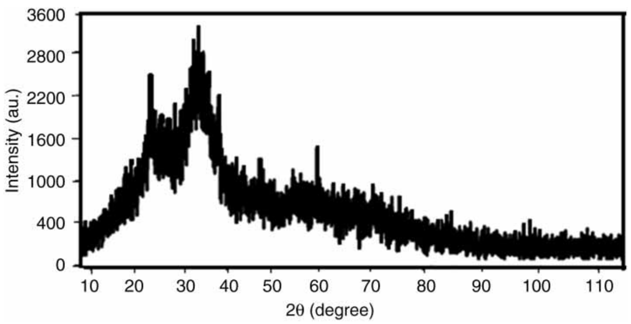


Figure 3 | XRD pattern of walnut green hull.

$$\text{PhOH} \rightleftharpoons \text{PhO}^- + \text{H}^+ [\text{pKa} = 10]$$

The ionic fraction of phenolate ion can be calculated from:

$$\varphi_{\text{ions}} = \frac{1}{1 + 10^{[\text{pk}_{\text{a}-\text{pH}}]}} \tag{1}$$

In a previous study, the potential of Tendu (Diospyros melanoxylon) leaf refuse to remove phenol from aqueous solution was studied. For this purpose, the Tendu leaf refuse was carbonized by subjecting it to chemical treatment using sulfuric acid. Batch experiments were carried out under varying experimental conditions of contact time, phenol concentration, adsorbent dose and pH. Several 100 mL portions of 100 mg L^{-1} of phenol solution were adjusted to the assigned pH with sodium hydroxide or sulfuric acid and were mixed with different adsorbent doses, with stirring for 1 h. Measurement of initial and final phenol concentration gave the percent adsorption of phenol. The adsorption of phenol by Tendu leaf refuse was studied at various pH values. The adsorbed amount decreased with increasing pH value, which can be attributed to the phenol ionization and the presence of hydroxyl ions on the adsorbent. In this study, the pH optimum of phenol adsorption on Tendu leaf refuse was obtained at 6.0 (Nagda & Diwan Ghole 2006).

The distribution of adsorbate molecules between the liquid phase and the solid phase can be expressed by the equilibrium adsorption isotherm that is an important step for the design of adsorption systems. Phenol adsorption data have been analyzed by using adsorption isotherm models such as the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D–R). The linear plots for the adsorption isotherms have been obtained using the following equations:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{1}{q_m} c_e \tag{2}$$

$$\log q_e = \log k_f + \frac{1}{n} \log c_e \tag{3}$$

$$q_e = BLnK_t + BLnC_e \tag{4}$$

$$\ln qe = \ln q_m - K_{DR}\varepsilon^2 \tag{5}$$

where C_e is the equilibrium concentration of adsorbate in solution (mg L^{-1}), q_e is the amount adsorbed at equilibrium (mg g^{-1}), q_m (the amount of ultimate adsorption capacity (mg g^{-1})) and b (energy of adsorption (L mg^{-1})) are the Langmuir constants that can be calculated from the slope and intercept of the linear plot of C_e versus C_e / q_e respectively. K_f and $1/n$ are the Freundlich constants related to adsorption capacity and adsorption intensity respectively that can be obtained from the intercept and slope of the linear plot of $\log q_e$ versus $\log c_e$. For favorable adsorption, n should have values lying in the range of 1 to 10. For the adsorption of phenol onto walnut green hull, the value of n was 2, therefore the adsorption mechanism is favorable. K_t is the equilibrium binding constant (L mg^{-1}) and B is the variation of adsorption energy (kJ mol^{-1}). K_t and B can be calculated from the slope and intercept of the linear plot of q_e versus Ln c_e (Han et al. 2008; Kuo et al. 2008). K_{DR} is a constant related to the mean free energy of sorption per mol of the sorbate (mg^2 kJ^{-2}) and ε is Polanyi potential (J mg^{-1}). K_{DR} can be calculated from the slope of the linear plot of ln q_e versus ε^2. Also, ε can be obtained using the following equation:

$$\varepsilon = RT\ln\left(1 + \frac{1}{C_e}\right) \tag{6}$$

where R is the universal gas constant (8.314 kJ/kmol.°K) and T (°K) is the absolute temperature. The mean free energy of adsorption (E) can be written as:

$$E = 1/[2K_{DR}]^{0.5} \tag{7}$$

If the value of E is between 8 and 16 kJ mol^{-1}, the adsorption process is chemical and if it is less than 8 kJ mol^{-1}, the adsorption process is physical (Behnamfard & Salarirad 2009). For the adsorption of phenol onto walnut green hull, the value of E was 10 kJ mol^{-1}, which indicates that the mechanism of phenol adsorption on adsorbent is chemical. The dimensionless separation factor (R_L) can describe the essential characteristics of the Langmuir isotherm that is presented in the following equation. The value of R_L describes the adsorption characteristics as shown in Table 2:

$$R_L = \frac{1}{[1 + bC_0]} \tag{8}$$

Table 2 | Langmuir isotherm dimensionless separation factor parameter (R_L)

Type of isotherm	**R_L value**
Unfavorable	$R_L>1$
Linear	$R_L = 1$
Irreversible	$R_L = 0$
Favorable	$0<R_L<1$

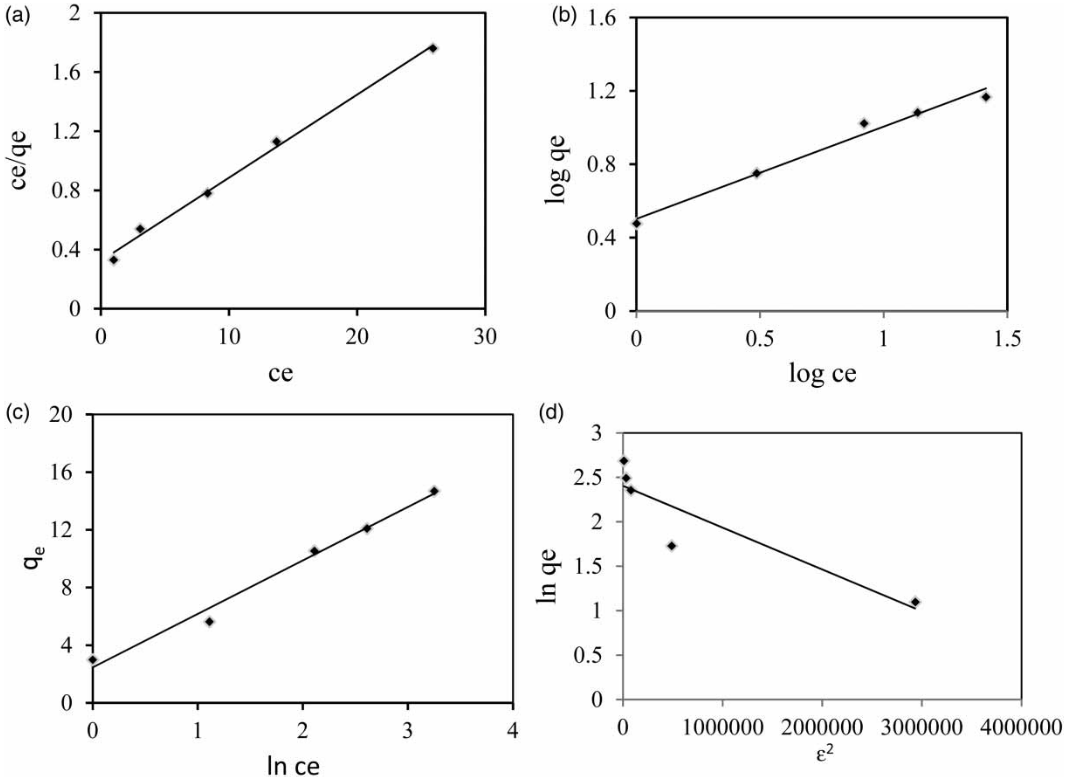


Figure 5 | Langmuir (a), Freundlich (b), Temkin (c), D–R (d) adsorption isotherms for the adsorption of phenol onto walnut green hull (temperature = 25 ± 1 °C, pH = 4, contact time = 48 h and adsorbent dose = 1 g L^{-1}).

The value of R_L calculated for phenol was 0.3; therefore adsorption of phenol onto walnut green hull is favorable. It was found that the Langmuir isotherm model fitted best the equilibrium data and was applicable with a maximum monolayer adsorption capacity of 17.8 mg g^{-1}. It is the most common isotherm equation to use, due to its simplicity and its ability to fit a variety of adsorption data. It is based on four assumptions:

1. All of the adsorption sites are equivalent and each site can only accommodate one molecule.
2. The surface is energetically homogeneous and adsorbed molecules do not interact.
3. There are no phase transitions.
4. At the maximum adsorption, only a monolayer is formed. Adsorption only occurs on localized sites on the surface, not with other adsorbents.

The linearized adsorption isotherms are shown in Figure 5. Table 3 shows the parameters of the Langmuir, Freundlich, Temkin and D–R isotherm models.

Table 3 | Isotherm parameters for phenol adsorption onto walnut green hull

Langmuir	
q_m (mg g^{-1})	17.8
b (L mg^{-1})	0.17
R_L	0.3
R^2	0.995
Freundlich	
K_F (mg g^{-1})	3.16
N	2
R^2	0.98
Temkin	
B (kJ mol^{-1})	3.70
k_t (L mg^{-1})	0.66
R^2	0.986
D–R	
q_m (mg g^{-1})	0.05
K_{DR} (mg^2 KJ^{-1})	11.63
E (KJ mg^{-1})	10
R^2	0.825

The kinetic study of phenol uptake by walnut green hull for different contact times was carried out using kinetic models such as the pseudo-first order, pseudo-second order, Elovich and intra-particle diffusion. The linear plots of the adsorption kinetics are shown in Figure 6. The linear plots for the adsorption kinetics of pseudo-first order, pseudo-second order, Elovich and intra-particle diffusion have been obtained using the following equations:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}\, t \tag{9}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}\, t \tag{10}$$

$$q_t = \left(\frac{1}{\beta}\right)\ln(\alpha\beta) + \left(\frac{1}{\beta}\right)\ln t \tag{11}$$

$$q_t = k_d t^{1/2} + I \tag{12}$$

where q_e (mg g^{-1}) and q_t refer to the amounts of adsorption at the equilibrium and any time t (min) respectively, k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the adsorption rate constants in the pseudo-first order adsorption and pseudo-second order adsorption respectively, k_1 (min^{-1}) can be calculated from the slope of the linear plot of log (q_e–q_t) versus t, and k_2 (g mg^{-1} min^{-1}) can be obtained from the intercept of the linear plot of t/q_t versus t (Pahlavanzadeh *et al.* 2010). The

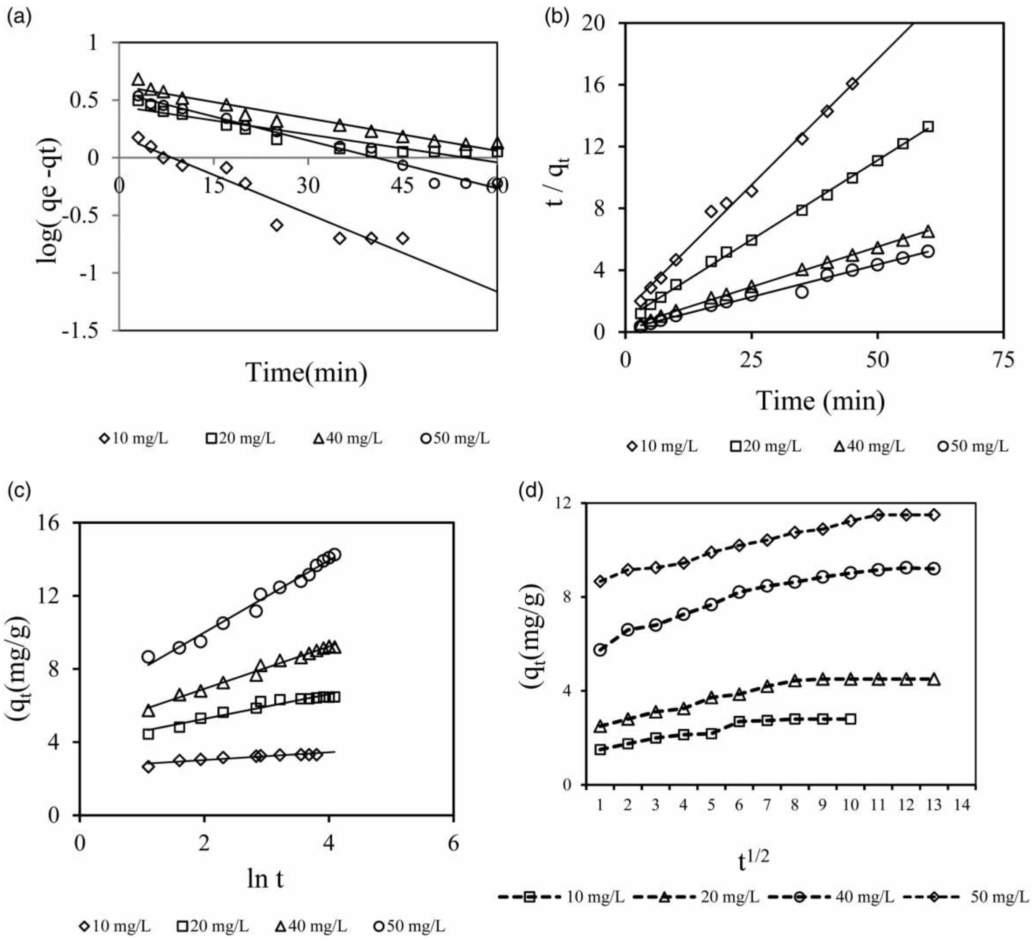


Figure 6 | Pseudo-first order (a), pseudo-second order (b), Elovich (c), intraparticle diffusion (d) kinetic models for the adsorption of phenol onto walnut green hull (temperature = 25 ± 1 °C, pH = 4, contact time = 2–60 min and adsorbent dose = 1 g L^{-1}).

Table 4 | Kinetic parameters for phenol adsorption onto walnut green hull at different initial concentrations

		Pseudo-first order			**Pseudo-second order**				**Elovich**			**Intra-particle diffusion**		
C_0 (mg/L)	**$q_{e,\,exp}$ (mg g^{-1})**	**$q_{e,\,cal}$ (mg g^{-1})**	**k_1 (min^{-1})**	**R^2**	**$q_{e,\,cal}$ (mg g^{-1})**	**k_2 (g mg^{-1} min^{-1})**	**h_0 (mg g^{-1} min^{-1})**	**R^2**	**A (mg g^{-1} min^{-1})**	**β (g mg^{-1})**	**R^2**	**k_d (mg g^{-1} min$^{-1/2}$)**	**I (mg g^{-1})**	**R^2**
10	3	1.54	0.05	0.921	3.07	0.072	0.67	0.993	3.3	2	0.95	0.25	1.2	0.92
20	5.64	2.77	0.018	0.884	5	0.048	1.2	0.998	6.9	1.35	0.97	0.34	2.1	0.92
40	10.55	4.2	0.029	0.948	10	0.03	3	0.998	12	1.1	0.98	0.54	5.3	0.94
50	12.1	5.4	0.02	0.98	12.04	0.03	4.34	0.989	14	1.06	0.98	0.64	7.9	0.98

initial adsorption rate, h_0 (mg g^{-1} min^{-1}) is determined as the following:

$$h_0 = k_2 {q_e}^2 \tag{13}$$

The parameter of α (mg g.min^{-1}) is the initial adsorption rate, and β (g mg^{-1}) is the rate desorption constant that can be calculated from the intercept and slope of the linear plot of q_t versus ln t respectively; k_d (mg g^{-1} min$^{-1/2}$) is the intra-particle diffusion rate constant (mg g^{-1} min$^{-1/2}$) that can be obtained from the slope of the linear plot q_t versus $t^{1/2}$ and I is a constant that gives an indication about the thickness of the boundary layer. The parameters of kinetic models are presented in Table 4. A small difference between $q_{e,\mathrm{exp}}$ and $q_{e,\mathrm{cal}}$, and also the R^2 value for all the experimental concentrations close to 1 indicated that the pseudo-second order model is the most suitable for phenol adsorption onto walnut green hull. Therefore, it can be stated that the rate of adsorption follows second-order chemisorptions and this model considers the rate limiting step as the formation of a chemisorptive bond involving sharing or exchange of electrons between the sorbate and the sorbent. Also, according to Table 4, the initial adsorption rate (h_0) increased with increasing initial phenol concentration, while the rate constant of adsorption (k_2) decreased.

The intra-particle diffusion model is to elucidate the diffusion mechanism. In many adsorption processes, an intra-particle diffusion model is the rate limiting step (if the plot of q_t versus $t^{1/2}$ is a straight line). Also, according to this model, if multi linear plots involve various steps, then two or more steps influence the adsorption process. In the present study, all the plots present multi-linearity, an initial curved portion (the faster adsorption stage of the curve may be considered as an external surface adsorption) is followed by a gradual adsorption (where the intra-particle diffusion is rate-controlled), and a plateau (intra-particle diffusion starts to slow down due to the extremely low adsorbate concentrations in the solution) (Aksu & Tunç 2005).

CONCLUSIONS

In this study, for an equilibrium isotherm and kinetic fitting of phenol adsorption experimental data onto the walnut green hull adsorbent, linear regression analysis was carried out. It was found that the Langmuir isotherm model fitted the equilibrium data best, and a maximum adsorption capacity of 17.8 mg g^{-1} was obtained. Also, a correlation coefficient greater than 0.99 indicated the applicability of a pseudo-second order adsorption model for phenol adsorption onto walnut green hull. The functional groups involved in adsorption of phenol onto walnut green hull included OH, C-O, C-H and C = O. Intra-particle diffusion is not the sole rate controlling factor, and the process may be controlled by external surface adsorption and intra-particle diffusion. The investigation shows a favorable adsorption site for phenol on the surface of walnut green hull, and shows that walnut green hull is a promising adsorbent for the removal of phenol from aqueous solutions.

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