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Removal Efficiency, Adsorption Kinetics and Isotherms of Phenolic Compounds from Aqueous Solution Using Rice Bran Ash

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In the present study, a porous rice bran ash powder was synthesized and tested for the removal of phenolic compounds from aqueous solution. The size of the rice bran ash particles was 14.49 nm, with a BET surface area of 50.14 m^2g^{-1}. Adsorption of phenol, 2-chlorophenol and 4-chlorophenol was conducted at various contact times, solution pHs, adsorbate concentrations and rice bran ash dosages in a batch reactor. Batch kinetic studies showed that an equilibration within 240 min could be achieved at pH as low as 5.0 ± 0.2 for the adsorption of 50 mg L^{-1} phenolic compounds concentration. Removal efficiency of 2-chlorophenol was lower than phenol and 4-chlorophenol. The phenol, 2-chlorophenol and 4-chlorophenol maximum removal efficiency was observed at an initial pH of 5 ± 0.2. Also the maximum predicted adsorption capacities were 4.6332, 3.6749 and 4.3060 mg g^{-1} for phenol, 2-chlorophenol and 4-chlorophenol, respectively. The capacity of phenol, 2-chlorophenol and 4-chlorophenol adsorption at equilibrium increased with the increase of initial concentration (50-400 mg L^{-1}) and decreased with the increase of adsorbent dosage (2.5-10 g L^{-1}). The isotherm evaluations revealed that the equilibrium data for 2-chlorophenol and 4-chlorophenol could be fitted with the Freundlich model, whereas the equilibrium data for phenol fitted with Langmuir model best. In addition, the adsorption kinetic data were found fit the test results well based on a pseudo-second-order rate for selected phenolic compounds.

Key Words: Rice bran ash, Phenolic compounds, Adsorption, Isotherms, Kinetics.

INTRODUCTION

Phenols and chlorophenols are contaminants in soils, sediments, surface waters and groundwater, because of their worldwide utilization in the last 50 years[1]. These compounds commonly entered to aqueous effluents from various manufacturing processes such as oil refineries, coke plants, adhesives, polyamide and phenolic resin plants[2,3]. Chlorophenol derivatives, especially 4-chlorophenol as a typical example of an environmentally significant compound, has been detected in several industries, such as wood preservatives, waste incineration, uncontrolled use of pesticides, fungicides and herbicides, as well as byproducts formed during bleaching of pulp with chlorine and in chlorination disinfection of drinking water[4-6]. Chlorophenols can also be produced by degradation of chlorinated pesticides, from the reaction of water with the phenols present in the environment and during the incineration of organic material in the presence of chlorine. These create an even more dangerous contamination[7]. Contamination of surface water and ground water with aromatic compounds such as phenolic compounds is one of the most serious environmental problems in recent years. These organic compounds are considered as pollutants with priority concern[8]. Wastewater containing phenolic compounds presents serious discharge problems due to their poor biodegradability, high toxicity and long term ecological damages. Because of high toxicity of phenols, they are strictly regulated and their industrial apply have been increasingly avoided by substituting them with harmless compounds. For drinking water, a guideline concentration of 1 mg L^{-1} has been prescribed (WHO 1994)[6] and also the environmental protection agency calls for lowering phenol content in the wastewater to less[9] than 1 mg/mL.

Due to the toxic properties of both phenol and chlorophenols[6,10], the efficient removal of these compounds from industrial aqueous effluents has a vast practical significance for environmental protection[6]. Biological degradation, activated carbon adsorption, solvent extraction, electrochemical methods and chemical oxidation are the most extensively used methods for removing phenols and its derivatives from wastewaters[11-15]. Problems such as high cost, little efficiency, continuous input of chemicals and generation of toxic byproducts are restrictive factors for wide applications of some of these remediation strategies[9,13]. Therefore, easy, useful, economic and ecofriendly techniques are required for fine tuning of effluent/wastewater treatment[16].

The search for a low cost and easily available adsorbent has led to the investigation of materials of agricultural. The rice bran is an agricultural waste, accounting for about one-fifth of the annual gross rice, 545 million metric tons, of the world[17] that 96 % of it is generated in developing countries[18] especially in Southeast[19]. Since the main components of rice bran are carbon and silica, that has high porosity and large surface area because it retains the skeleton of cellular structure and it has the potential to be used as an adsorbent[20] and utilization of this source of mass would solve both disposal problem and access to cheaper material for adsorption in water pollutants control system[18].

In the present investigation, the rice bran ash efficiency for removing phenol, 2-chlorophenol and 4-chlorophenol from aqueous solution was studied. The influences of various factors, such as contact time, initial pH, initial pollutant concentrations and sorbent dosage on the adsorption capacity were also studied. The Freundlich, Langmuir and Temkin models were used to analyze the adsorption equilibrium. Also, the test data were correlated using three kinetic models, Pseudo-first-order, Pseudo-second-order and Weber-Morris Intraparticle diffusion kinetic models.

EXPERIMENTAL

Preparation of rice bran ash: The rice bran was obtained from the north area of Iran (Babol, Iran). The proximate and ultimate analysis of rice bran is shown in Table-1. For preparation of rice bran ash, at first, rice brans were crushed, sieved and thoroughly washed with distilled water to remove all dirt and were dried at 105 ºC for 2 h till constant weight. Then, the rice brans were burned at temperature of 400 ºC (RBA-400) for 2 h in a muffle furnace. The heating rate was 25-35 ºC min^{-1}. Finally, the rice bran ashes were powdered and stored in desiccators until they were used[18,20,21]. Physical and chemical composition of the mineral ash has been listed in Table-2.

TABLE-1
PROPERTIES OF THE RICE BRANS[18, 20, 21]

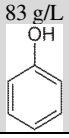
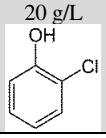
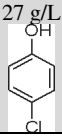
Proximate analysis (wt %)		Ultimate analysis (wt %)		Component analysis (wt %)	
Volatiles	59.5	Carbon	44.6	Cellulose	34.4
Moisture	7.9	Hydrogen	5.6	Hemicellulose	29.3
Ash	17.1	Oxygen	49.3	Lignin	19.2
				Ash	17.1

TABLE-2
PHYSICAL AND CHEMICAL CHARACTERISTICS OF RICE BRAN ASH[18,20,21]

Property	RHA
Colour	Grey
Carbon (%)	1.88
Silicon dioxide (%)	79.27
pH	9.92
SiO_2, (%)	96.34
K_2O (%)	2.31
MgO (%)	0.45
Al_2O_3 (%)	0.41
CaO (%)	0.41
Fe_2O_3 (%)	0.2
Average pore diameter (nm)	14.49
Total pore volume (mg L^{-1})	0.182
BET surface area (m^2 g^{-1})	50.14
Particle size (mm)	Powdered

Phenolic solution: The phenolic compounds used in this study were phenol, 2-chlorophenol (2-CP) and 4-chlorophenol (4-CP). Some of the important physicochemical properties of the selected phenolic compounds are given in Table-3. All these purchased chemicals from Merck Co. (> 98 %, Germany), were used without further purification. A stock solution was prepared by dissolving 1 g of phenol, 2-chlorophenol or 4-chlorophenol, in deionized distilled water and dilute to 1000 mL. The phenolic solutions for the adsorption experiments were prepared by diluting the stock solution to give different concentrations within the range of 50 to 400 mg L^{-1} for phenol and chlorophenols. All stock solutions were preserved in a covered dark bottle till used.

TABLE-3
BASIC PROPERTIES OF THE INVESTIGATED PHENOLIC COMPOUNDS

Characteristic	Phenol	2-Chloro-phenol	4-Chloro-phenol
Chemical formula	C_6H_6O	C_6H_5OCl	C_6H_5OCl
Class	Phenols	Phenols	Phenols
C.I. number	108-95-2 [Y]	95-57-8 [Y]	106-48-9
Molecular weight (g mol^{-1})	94.11	128.56	128.56
Water solubility (20 ºC)	83 g/L	20 g/L	27 g/L
Molecular structure			

Surface morphology of adsorbent: Surface morphology of the produced adsorbent (rice bran ash) were investigated using scanning electron microscopy (Fig. 1). The sample was placed on the aluminium tub and coated with gold for electron reflection. The sample was then vacuumed for 5-10 min prior to analysis.

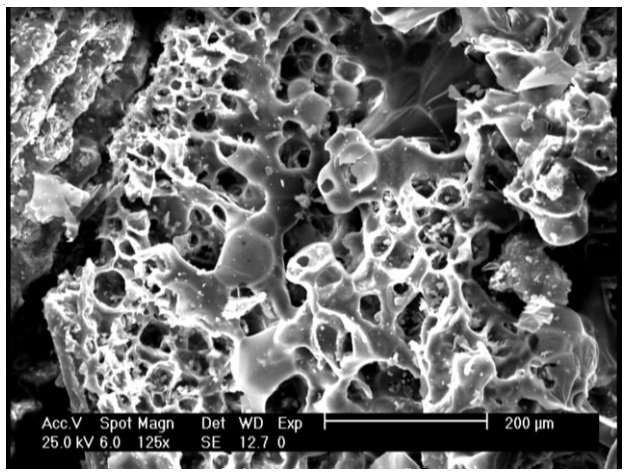


Fig. 1. SEM image of rice bran ash (125×)

Analysis of phenolic compounds: The concentration of phenol, 2-chlorophenol and 4-chlorophenol, in aqueous solution were determined by measuring absorbance at λ_{max} (wavelength 269.5 nm, 274 nm and 280 nm) respectively, using 10 mm quartz cells in a spectrophotometer UV/VIS (CECIL EC 7400, England)[3]. Also, the ionic strength of the phenol solutions was maintained constant during the adsorption experiments. Control and parallel tests were conducted. It was

observed that phenol, 2-chlorophenol and 4-chlorophenol adsorption on the flask walls and its release from rice bran ash could be negligible.

Kinetic experiments: The experimental design for this study was one factor at a time. Adsorption studies were conducted in a routine manner by the batch technique. Preliminary tests were carried out in order to determine the equilibrium time for each adsorbate. For this purpose, 0.4 g of rice bran ash was added to 40 mL phenol solution with a known concentration (50 mg L^{-1}) and initial pH 5 in 100 mL Erlenmeyer flasks. The flasks placed on a rotating shaker (Heidolph Unimax 2010, Germany) with constant agitation, 150 rpm, at 21 ± 2 ºC. The pH of solutions during the contact period (5-300 min) was adjusted at 5 ± 0.2 using small amount of 0.01 N HCl and 0.01N NaOH as required. All pH measurements were carried out with a pH meter (HQ40d, USA). Samples are filtered through filter papers (Whatman No. 41 ashless) and the phenol or chlorophenols concentration was determined using spectrophotometer. At the end of this stage according to the results, kinetic equations were carried. Also, the effect of pH values (2-11), initial phenol, 2-chlorophenol or 4-chlorophenol concentration (50-400 mg L^{-1}) and adsorbent dose (0.1-0.4 g 40 mL^{-1}) on the adsorption of phenolic compounds by rice bran ash was studied.

Equilibrium experiments: In this stage, were paid to equilibrium isotherms with rice bran ash dose change (0.1-0.4 g 40 mL^{-1}) and optimized amounts of contact time, pH and initial phenolic compounds concentration factors. Finally the equilibrium adsorption and equilibrium capacity were discussed. In order to description of relation between amount of each phenolic compounds and sorbent dosage, was used three Langmuir, Freundlich and Temkin models.

Data evaluation: The removal efficiency (IE) and adsorption capacity (q_e) of the rice bran ash determined from the concentration difference of the solution, at the beginning and at equilibrium:

$$E(\%) = \frac{(C_0 - C_f)}{C_0} \times 100 \quad (1)$$

$$q_e = \frac{V}{m} \times (C_0 - C_e) \quad (2)$$

where, E is removal efficiency, C_o (mg L^{-1}) is the initial concentrations of phenolic solutions, C_f (mg L^{-1}) is the concentration after adsorption time, q_e (mg g^{-1}) is the adsorption capacity at equilibrium time and C_e (mg L^{-1}) denote equilibrium concentrations of phenolic solutions, V(L) is the volume of the solution and m(g) is the mass of the adsorbent used[22].

Validity of adsorption isotherm: Apart from correlation coefficient (R^2), Marquardt's percent standard deviation (MPSD) and the hybrid error function (HYBRID) were also used to measure the goodness-of-fit. Marquardt's percent standard deviation and HYBRID can be defined as:

$$MPSD = 100\sqrt{\frac{1}{N-p}\sum_{i=1}^{N}\left(\frac{q_{ei}^{exp} - q_{ei}^{cal}}{q_{ei}^{exp}}\right)^2} \quad (3)$$

$$HYBRID = \frac{100}{N-p}\sum_{i=1}^{N}\left[\frac{\left(q_{ei}^{exp} - q_{ei}^{cal}\right)^2}{q_{ei}^{exp}}\right] \quad (4)$$

where, q_{ei}^{exp} is the observation from the batch experiment i, q_{ei}^{cal} is the estimate from the isotherm for corresponding q_{ei}^{exp}, n is the number of observations in the experimental isotherm and p is the number of parameters in the regression model. The smaller Marquardt's percent standard deviation and HYBRID values indicate more accurate estimation of q_e value[23]. Marquardt's percent standard deviation and HYBRID functions were used in addition to R^2 because the number of parameters in the regression model (*i.e.*, p parameter) is effective in them.

Validity of kinetic models: The applicability of the models is verified through normalized standard deviation (NSD) and average relative error (ARE) factor between the experimental data and the model estimates of adsorption capacities and used to predict the adsorption of phenol, 2-chlorophenol and 4-chlorophenol behaviours. The mathematical equations of normalized standard deviation and average relative error given in eqns. (5) and (6):

$$NSD = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}\left[\frac{q_t^{exp} - q_t^{cal}}{q_t^{exp}}\right]^2} \quad (5)$$

$$ARE = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{q_e^{exp} - q_e^{cal}}{q_e^{exp}}\right| \quad (6)$$

where, q_t^{exp} and q_t^{cal} (mg g^{-1}) are experimental and calculated amount of chlorophenol compounds adsorbed on rice bran ash at time t and N is the number of measurements made. The smaller normalized standard deviation and average relative error values indicate more accurate estimation of q_t values[23,24].

RESULTS AND DISCUSSION

Effect of contact time: The data for the adsorption of phenol, 2-chlorophenol and 4-chlorophenol *versus* contact time at 50 mg L^{-1} initial concentration with 0.4 g 40 mL^{-1} of rice bran ash were obtained in pH value of 5 ± 0.2 (Fig. 2). Study showed that with contact time increasing and concentration reduction of phenolic compounds gradually increased the removal efficiency and after the contact time of 2 h, the removal was roughly constant till equilibrium was attained. 2-Chlorophenol showed lowest removal efficiency. These results also demonstrated that 90.7 % of phenol, 63.5 % of 2-chrophenol and 85.3 % of 4-chlorophenol were obtained in the first 60 min. Therefore, for considering economical view point 60 min as equilibrium time were selected. Kumar, *et al.*[2] acquired an equilibrium time 240 min for phenol, 2-chlorophenol and 4-chlorophenol on a natural sorbent. Also Aksu and Yener proposed the activation of the aromatic ring of monochlorophenols by the chlorine, which causes the existence of donor-acceptor interactions between the phenolic compounds and the groups of the sorbent outside. They also established that the adsorption of 4-chlorophenol is upper than of 2-chlorophenol and the arrangement of the -Cl atom in the benzene ring, in relation to phenolic -OH substituent, powerfully influences the adsorption[25]. The higher adsorption rate at the initial period (first 60 min) may be due to an increased number of vacant sites on the adsorbent available at the initial stage. As a result, a concentration gradient exists between

adsorbate in solution and adsorbate on adsorbent surface[26]. Maximum adsorption capacity of phenol, 2-chlorophenol and 4-chlorophenol by rice bran ash was found 4.6332, 3.6668 and 4.3060 mg g^{-1} adsorbent, respectively.

Effect of pH: For this purpose results showed that the adsorption process was highly depend on pH. This parameter could be influenced on surface characteristic, ionization degree and removal efficiency. Experiments demonstrated that maximum removal was obtained in pH = 5 for all compounds and for pHs lower than 5 and with further slope for more than 5, reduces removal percent and this is more for phenol (Fig. 3). These results were compatible with other studies[18,20].

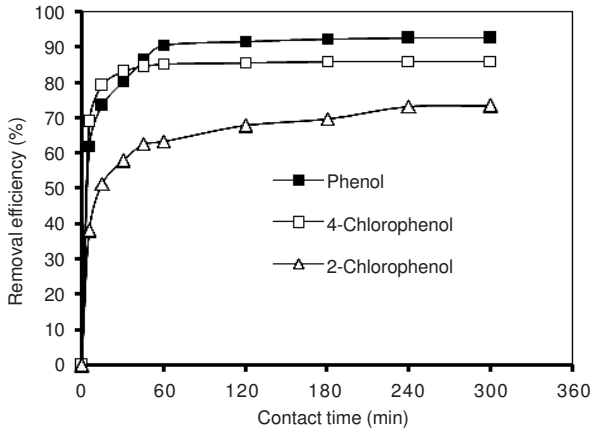


Fig. 2. Effect of contact time on the removal of phenol, 2-chlorophenol and 4-chlorophenol by rice bran ash (initial phenolic concentration = 50 mg L^{-1}, initial pH = 5 and adsorbent dose = 0.4 g 40 mL^{-1})

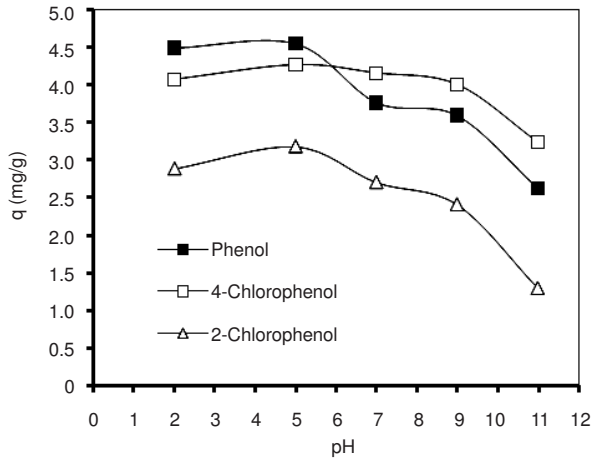


Fig. 3. Effect of pH on the removal of phenol, 2-chlorophenol and 4-chlorophenol by rice bran ash (initial phenolic concentration = 50 mg L^{-1}, contact time = 60 min and adsorbent dose = 0.4 g 40 mL^{-1})

Phenol and chlorophenols, being weakly acidic, partially ionizes in solution[26,27]. These ions are negatively charged and are directly attracted to the surface of rice bran ash by electrostatic force. Unionized phenol molecules would also be attracted, possibly, by physical force. At high pH, phenols form salts which readily ionize leaving negative charge on the phenolic groups and OH^- ions would compete with the phenol molecules for adsorption sites. Adsorption of excess of OH^- ions could convert an initial positively charged surface of rice bran ash into a negatively charged surface resulting repulsion of negatively charged phenoxide ions and therefore adsorption decreased[20,26]. The chloride (-Cl) ion on the benzene ring, which increases the acidic character, is responsible for forming anion on the oxygen atom of the OH group and also has a strong affinity for silica surfaces[28]. In other words, at high pH, the results indicated negative effect of pH on the adsorption of phenolic compounds on rice bran ash. With increasing pH, the built-up negative charges on both the adsorbate and adsorbent result in Coulomb's repulsion and consequently the lower adsorption of phenols. At lower pH values, the uptake of phenolic compounds is low due to the presence of H^+ ions suppressing the ionization of phenolic compounds and hence their uptake on polar sorbent are reduced[20,29]. The adsorption capacity decreasing above pH 5 may be due to electrostatic repulsion between the negatively charged adsorbent and sorbate and the donor-acceptor interactions between the aromatic ring activated by the -OH and -Cl substituent and the groups of the sorbents surface[2,9].

Effect of phenolic compounds concentration: The effect of concentration on removal efficiency and adsorption capacity was studied at pH = 5, 0.4 g 40 mL^{-1} of rice bran ash, 60 min contact time and concentrations from 50 to 400 mg L^{-1} (50, 100, 200, 300 and 400 mg L^{-1}). Results represented that increasing the concentration from 50 mg L^{-1} to 400 mg L^{-1}, decreased the removal efficiency to 45.66, 38.07 and 53.91 % for phenol, 2-chlorophenol and 4-chlorophenol, respectively. Increasing in initial phenolic compounds concentration increases the mass transfer driving force that overcome to adsorbate mass transfer resistances in the aqueous solid phase and therefore more phenol molecules pass through the bulk solution to the particle surface[20,27]. At low phenolic compounds concentrations the ratio of surface active sites to the total phenols molecules in the solution is high and hence all phenols molecules may interact with the rice bran ash and be removed from the solution[30]. The absorption capacity can be increased by increasing the concentration due to a higher probability of collision between the chlorophenol molecules and sorbent[27].

While for concentration of 400 mg L^{-1} in terms of q_{eq}, the q_{eq} of 4-chlorophenol (q_{eq} = 21.56 mg g^{-1}) is more than phenol (q_{eq} = 18.26 mg g^{-1}) and 2-chlorophenol (q_{eq} = 15.22 mg g^{-1}) (Fig. 4). It was possibly due to the higher solubility of phenol in water[2]. These results were the same as of other studies[25].

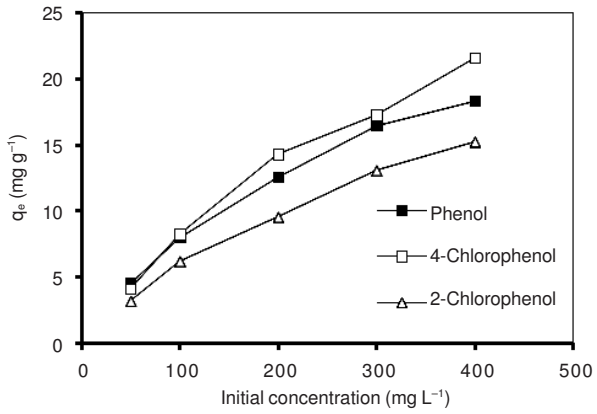


Fig. 4. Effect of initial phenolic concentration on adsorption capacity by rice bran ash (contact time = 60 min, pH = 5 and adsorbent dose = 0.4 g 40 mL^{-1})

Effect of adsorbent dosage: The Effect of different rice bran ash dosages on phenol, 2-chlorophenol and 4-chlorophenol removal efficiency were presented in Fig. 5. As it was accepted, with dose decreasing, adsorption ratio reduced due to the availability of a greater number of active sites on the sorbent[2]. It can also be seen from figure that the uptake of solute markedly increased up to a sorbent dose and thereafter the ratio of increasing in removal is gradually decreased. In other similar studies that have been conducted, same results obtained[9,31].

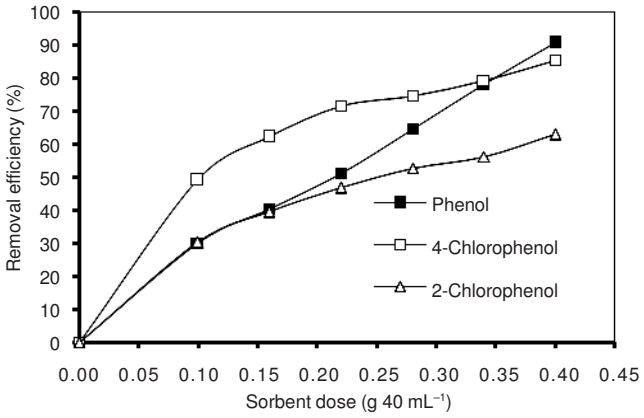


Fig. 5. Effect of sorbent dose on the removal of phenol, 2-chlorophenol and 4-chlorophenol (contact time = 60 min, pH = 5 and initial phenolic concentration = 50 mg L^{-1})

Adsorption isotherm models: Information has been provided on the capacity of the adsorbent by equilibrium studies. An adsorption isotherm is characterized by certain constant values. These values express the surface properties and affinity of the adsorbent and can also be used to compare the adsorptive capacities of the adsorbent for different pollutants. The Langmuir, Freundlich and Temkin models are from the most frequently used models. So, the equilibrium adsorption data of phenol, 2-chlorophenol and 4-chlorophenol onto rice bran ash adsorbent were analyzed using them. Linear regression analyses of these models and a comparison of their correlation coefficient (R^2), Marquardt's percent standard deviation and HYBRID can be used for selection of the best fit isotherm[31].

The Langmuir adsorption model describes monolayer adsorption of adsorbate onto a homogeneous adsorbent surface. Moreover, there is negligible interaction between the adsorbed molecules and adsorption sites having uniform energies. The linear form of the Langmuir isotherm equation [type (I)] can be described as[32,33]:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (7)$$

where, q_e and C_e are parameters that are described in eqn. 2, q_m is the maximum amount of adsorption (mg g^{-1}) and b is the adsorption equilibrium constant (L mg^{-1})[32,33].

The essential feature of the Langmuir isotherm can be described with dimensionless separation factor or equilibrium constant R_L that is used for the description of the adsorption condition[32-35]:

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

where, R_L is separation factor or equilibrium parameter, C_o (mg L^{-1}) is the initial amount of adsorbate and b (L mg^{-1}) is the Langmuir constant described above. The R_L parameter is considered as more reliable indicator of the adsorption. The adsorption process can be defined as irreversible (R_L = 0), favourable (0 < R_L < 1), linear (R_L = 1) or unfavourable (R_L >1) in terms of R_L[32,33]. Based on the Langmuir constant, the value of this parameter for phenol adsorption within rice bran ash (Table-4) is 0.0645, which confirms that the adsorption of phenols with on rice bran ash is favourable under the conditions of this study. It could be derived that the Langmuir isotherm gave better fits than the other isotherms for adsorption of phenol, where the maximum uptake capacity (q_m) for phenol is 5.903 mg g^{-1} (Table-4).

TABLE-4
ISOTHERMS PARAMETERS BY LINEAR REGRESSION METHOD FOR THE ADSORPTION OF PHENOL, 2- CHLOROPHENOL AND 4-CHLOROPHENOL BY RICE BRAN ASH

Isotherms	R^2	MPSD	HYBRID	Parameters
Phenol				
Freundlich	0.4468	9.03	4.29	n = 10.3521, K_F = 3.711 mg g^{-1} (L mg^{-1})$^{1/n}$
Langmuir	0.9499	8.74	4.10	q_m = 5.903 mg g^{-1}; b = 0.289L mg^{-1}, R_L = 0.0645
Temkin	0.4263	15.17	10.90	q_m = 0.494mg g^{-1}; K_T = 1200.4 L mg^{-1}
2-Chlorophenol				
Freundlich	0.9659	5.08	0.955	n = 0.9398, K_F = 0.1311 mg g^{-1} (L mg^{-1})$^{1/n}$
Langmuir	0.1475	197.18	1634.6	q_m = 51.81 mg g^{-1}; b = 0.002L mg^{-1}, R_L = 0.90
Temkin	0.9384	8.20	2.44	q_m = 4.614mg g^{-1}; K_T = 0.097 L mg^{-1}
4-Chlorophenol				
Freundlich	0.9542	7.68	3.04	n = 1.4069, K_F = 0.947 mg g^{-1} (L mg^{-1})$^{1/n}$
Langmuir	0.6933	10.72	5.87	q_m = 27.70 mg g^{-1}; b = 0.022L mg^{-1}, R_L = 0.47
Temkin	0.9242	12.78	8.01	q_m = 4.629 mg g^{-1}; K_T = 0.286 L mg^{-1}

The empirical Freundlich model is based upon the assumption of multilayer formation of adsorbate on the heterogeneous solid surface of the adsorbent and assumes that the stronger binding sites are occupied first and that the binding strength decreases with the increasing degree of site occupation[32,34]. A linear form of the Freundlich isotherm equation expression can be obtained by taking a logarithm:

$$\log(q_e) = \log(K_F) + \frac{1}{n}\log(C_e) \quad (9)$$

where constants K_F and n indicate the adsorption capacity and the adsorption intensity, respectively. The lower fractional value of n [0 < n < 1] indicates that weak adsorptive forces are effective on the surface of rice bran ash and the number of adsorption sites on the ash surface is limited and the adsorbed phenols may hinder the further adsorption of phenols[24].

The Temkin model considered the effects of some indirect adsorbate/adsorbate interactions on adsorption isotherms. As a result of adsorbate/adsorbate interactions, the heat of adsorption of all the molecules in the layer would decrease linearly

with coverage[24]. The linear form of the Temkin isotherm is represented by the following equation[24,32].

$$q_e = q_m \ln K_T + q_m \ln C_e \quad (10)$$

In this model, K_T is the binding constant which represents the maximum binding energy (L mg^{-1}) and q_m is the maximum amount of adsorption (mg g^{-1})[23,24].

The parameters of Langmuir and Freundlich models were determined with plots of C_e/q_e *versus* C_e and log q_e *versus* log C_e. For the analysis of data with the Temkin model, the parameters of equation have been determined with plot of q_e *versus* ln C_e[24]. The values of the parameters and the correlation coefficients, Marquardt's percent standard deviation (MPSD) and the hybrid error function (HYBRID) obtained are listed in Table-4. The applicability of the isotherm equations to describe the adsorption process was judged by the correlation coefficients, R^2 values. This indicates that the adsorption of phenol on rice bran ash is better described by the Langmuir model than the other two models, whereas the equilibrium data for 2-chlorophenol and 4-chlorophenol fitted with the Freundlich model best (Table-4). Between different linear types of Langmuir model, type (I) best represent the equilibrium data. This in turn suggests that adsorption occurs as the monolayer phenol adsorb onto the homogenous adsorbent surface. The Freundlich isotherm model fitted the experimental data better than Langmuir and Temkin isotherm models for the adsorption of 2-chlorophenol and 4-chlorophenol, also suggested that the surface of rice bran ash for adsorption of 2-chlorophenol and 4-chlorophenol is heterogeneous. Furthermore, multilayer adsorption of 2-chlorophenol and 4-chlorophenol has been proposed by Freundlich isotherm model. As shown in Table- 4, the value of 1/n [n > 1] for 4-chlorophenol represents a favourable adsorption condition and the lower fractional value of n [n < 1] for 2-chlorophenol indicates that weak adsorptive forces are effective on the surface of rice bran ash and the number of adsorption sites on the ash surface is limited and the adsorbed 2-chlorophenol may hinder the further adsorption of that. In other words, the adsorbed 2-chlorophenol is bound to the surface with weaker and weaker free energies[24]. The related plots are shown in Figs. 6 and 7. Owing to the similarity of the adsorbent used in all experiments carried out during this study, the difference in adsorption removal and capacity of phenol, 2-chlorophenol and 4-chlorophenol may be attributed to their chemical structure and properties. From an engineering perspective, obtaining relatively high removal efficiency, in addition to acidic optimum adsorption pH for phenol, 2-chlorophenol and 4-chlorophenol, as well as the short contact time required, present the prepared rice bran ash powder as an attractive and promising alternative for phenolic compounds removal in practical applications.

Adsorption kinetic modelling: The adsorption kinetics is one the most important data in order to understand the mechanism of the adsorption and to assess the performance of the adsorbents. Different kinetic models including the Lagergren's pseudo-first-order, pseudo-second-order and Weber-Morris intraparticle diffusion models were applied for the experimental data to predict the adsorption kinetics. The linear form of the pseudo-first-order equation by Lagergren[31] is given as eqn. 11:

$$\ln(q_{eq} - q_t) = \ln q_{eq} - \frac{K_1 t}{2.303} \quad (11)$$

where, q_{eq} and q_t (mg g^{-1}) are the amounts of adsorption capacity at equilibrium at time t, respectively and k_1 (min^{-1}) is the rate constant of pseudo-first-order adsorption. Experimental data were plotted in form of $\ln(q_{eq}-q_t)$ against time to evaluate the suitability of the pseudo-first-order model line in Fig. 8. The values of k_1 and the calculated $q_{eq.cal}$ were obtained from slope and intercept of straight line in Fig. 8. These values along with the corresponding correlation coefficient (R^2), average relative error and normalized standard deviation were shown in Table-5. The value $q_{eq.cal}$ determined from the model is not in good agreement with the experimental value of $q_{eq.exp}$ (4.5337, 3.1747 and 4.2639 mg g^{-1} for phenol, 2-chlorophenol and 4-chlorophenol, respectively). Therefore the Lagergren's pseudo-first-order model is not suitable to adsorption of phenol, 2-chlorophenol and 4-chlorophenol onto the rice bran ash.

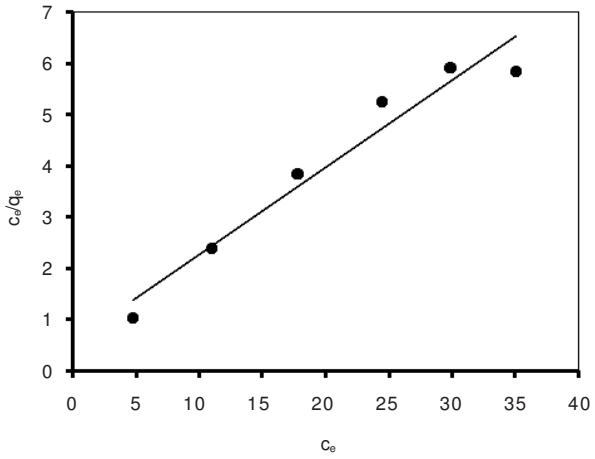


Fig. 6. Linearized Langmuir isotherm for phenol adsorption by RBA (Adsorbent dosage = 2.5-10 g L^{-1}, pH = 5 and initial phenol concentration = 50 mg L^{-1})

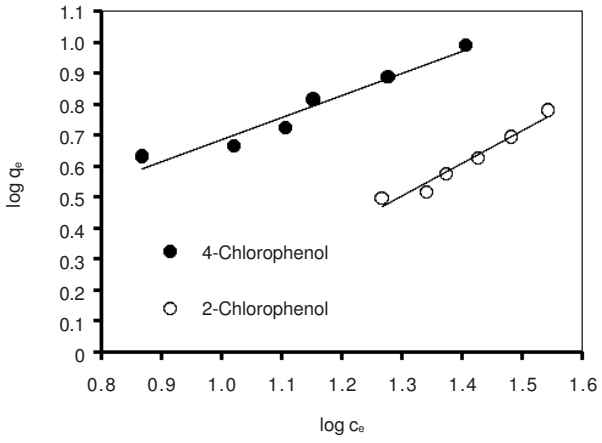


Fig. 7. Linearized Freundlich isotherm for 2-chlorophenol and 4-chlorophenol adsorption by rice bran ash (adsorbent dosage = 2.5-10 g L^{-1}, pH = 5 and initial 4-chlorophenol concentration = 50 mg L^{-1}

The pseudo second-order model [type (I)] is more suitable for the description of the kinetic behaviour of adsorption in which chemical adsorption is the rate-controlling step. This equation is in the following form[32]:

TABLE-5
KINETIC MODELS PARAMETERS BY LINEAR REGRESSION METHOD FOR THE ADSORPTION OF PHENOL, 2-CHLOROPHENOL AND 4-CHLOROPHENOL BY RICE BRAN ASH

Kinetic models	R^2	NSD	ARE	Parameters
		Phenol		
Pseudo-first order	0.9459	79.72	74.62	q_e = 1.559 mg g^{-1}; k_1 = 0.0284 h^{-1}
Pseudo-second order	0.9999	4.32	0.38	q_e = 4.739 mg g^{-1}; k_2 = 0.0618 g mg^{-1} h^{-1}
Intraparticle diffusion	0.5247	15.47	7.02	k_p = 0.180 mg g^{-1} $h^{-0.5}$; C = 2.347
		2-Chlorophenol		
Pseudo-first order	0.8843	66.50	60.69	q_e = 1.971 mg g^{-1}; k_1 = 0.0194 h^{-1}
Pseudo-second order	0.9992	10.62	3.22	q_e = 3.736 mg g^{-1}; k_2 = 0.0304 g mg^{-1} h^{-1}
Intraparticle diffusion	0.6736	14.30	6.35	k_p = 0.158 mg g^{-1} $h^{-0.5}$; C = 1.46
		4-Chlorophenol		
Pseudo-first order	0.8375	105.99	99.93	q_e = 0.587 mg g^{-1}; k_1 = 0.0266 h^{-1}
Pseudo-second order	1.0000	1.09	0.4	q_e = 4.384 mg g^{-1}; k_2 = 0.2095 g mg^{-1} h^{-1}
Intraparticle diffusion	0.3799	16.18	7.27	k_p = 0.144 mg g^{-1} $h^{-0.5}$; C = 2.581

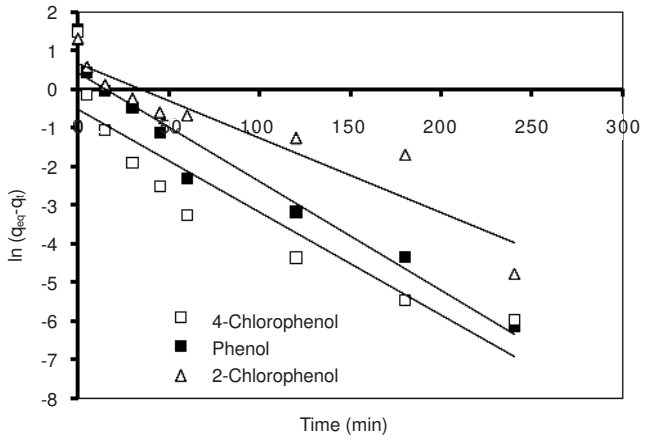


Fig. 8. Lagergren's pseudo-first-order kinetic model for adsorption of phenol, 2-chlorophenol and 4-chlorophenol

$$\frac{t}{q_t} = \frac{1}{K_2 q_{eq}^2} + \frac{t}{q_{eq}} \quad (12)$$

where, q_{eq} and q_t (mg g^{-1}) are the adsorption capacity at equilibrium and at time, respectively and k_2 (g mg^{-1} min^{-1}) is the rate constant of pseudo-second-order adsorption. Experimental data were plotted in form of t/q_t *versus* time to show the suitability of the pseudo-second-order kinetic model in Fig. 9. The values of $q_{eq,cal}$ and the calculated k_2 were obtained from slope and intercept of straight line in Fig. 9.[35,36]. These values along with the corresponding correlation coefficient (R^2), average relative error and normalized standard deviation were shown in Table-5. The correlation coefficient (R^2) for the pseudo-second-order equation is high and the calculated $q_{eq,cal}$ value agrees with the experimental $q_{eq,exp}$ (4.5337, 3.1747 and 4.2639 mg g^{-1} for phenol, 2-chlorophenol and 4-chlorophenol, respectively) and lower values of average relative error and normalized standard deviation confirm these results.

The kinetic results can be used to test the presence or absence of intraparticle diffusion and to determine whether intraparticle diffusion is the rate-limiting step for adsorption. The Weber-Morris intraparticle diffusion models can be expressed as[2,30]:

$$q_t = k_{int} t^{1/2} + C \quad (13)$$

where, q_t (mg L^{-1}) is the amount adsorbed at time t (min) and K_{int} is the constant of intraparticle diffusion rate (mg g^{-1} $min^{-1/2}$). C is the value of the intercept, which gives an idea about the boundary layer thickness, *i.e.*, the larger the intercept; the greater is the boundary layer effect. The plots of q_t *vs.* $t^{1/2}$ obtained for the adsorption of phenol, 2-chlorophenol and 4-chlorophenol onto rice bran ash at different times are shown in Fig. 10, respectively. The intraparticle rate constant K_{int} (mg g^{-1} $min^{-1/2}$) and intercept C (mg g^{-1}) are given in Table-5. The results indicated that intraparticle diffusion cannot be accepted as a rate-controlling step for the adsorption of adsorbates onto rice bran ash due to the fact that the values of correlation coefficients (R^2), average relative error and normalized standard deviation for the intraparticle diffusion model are not suite in comparing to with pseudo-second-order and pseudo-first-order kinetic models (Table-5). So, according to the results, adsorption rates of phenol, 2-chlorophenol and 4-chlorophenol onto the rice bran ash can be more appropriately described using pseudo-second-order kinetic model.

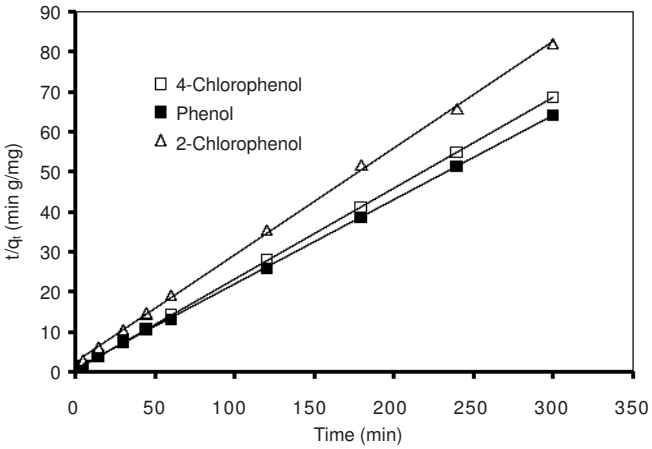


Fig. 9. Pseudo-second-order kinetic model for adsorption of phenol, 2-chlorophenol and 4-chlorophenol

Conclusion

In this study, a porous rice bran ash powder was produced and tested as a novel adsorbent for the removal of phenolic compounds (phenol, 2-chlorophenol and 4-chlorophenol). The effects of rice bran ash dosage, initial pH, contact time and initial adsorbate concentration on the removal of phenol, 2-chlorophenol and 4-chlorophenol were investigated separately through batch experiments. Results indicated that the synthesized powder could effectively remove high concentrations of

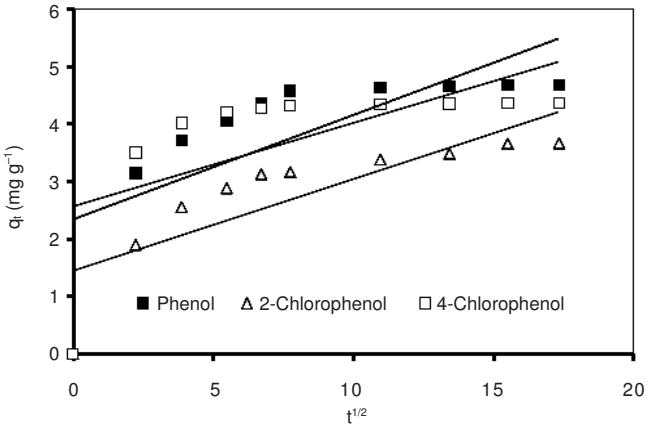


Fig. 10. Intraparticle diffusion model for adsorption of phenol, 2-chlorophenol and 4-chlorophenol

phenol and 4-chlorophenol in a short contact time. But removal rate of 2-chlorophenol was lower than phenol and 4-chlorophenol. The optimum dosage, pH and contact time were obtained to be 2.5 g L-1, pH 5 and 60 min for the adsorption of 50 mg L^{-1} phenolic compounds concentration, respectively. Isotherm modeling revealed that the Langmuir equation could better describe the adsorption of phenol onto the rice bran ash as compared to other models, whereas the equilibrium data for 2-chlorophenol and 4-chlorophenol fitted with Freundlich model best. Kinetic data were appropriately fitted with the pseudo-second-order adsorption rates. Because of the high specific surface area and nano-scale particle size, rice bran ash indicated favourable adsorption behaviour for phenol, 2-chlorophenol and 4-chlorophenol. Rice bran ash is a non-toxic material and can be made in a simple and cost-effective way for simple application. These unique features present rice bran ash as a novel, promising and feasible alternative for phenolic compounds removal.

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