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Kinetic, isotherms and thermodynamic studies in the removal of 2-chlorophenol from aqueous solution using modified rice straw

Davoud Balarak[a], Edris Bazrafshan[a], Yousef Mahdavi[b,*], Lalhmunsiama[c], Seung-Mok Lee[c,*]

[a]*Department of Environmental Health, Health Promotion Research Center, School of Public Health, Zahedan University of Medical Sciences, Zahedan, Iran, Tel. +98-9388517121; email: dbalarak2@gmail.com (D. Balarak), Tel. +98-9149082245; email: ed_bazrafshan@yahoo.com (E. Bazrafshan)*
[b]*Departmentof Environmental Health engineering, Student Research Committee, Mazandaran University of Medical Sciences, Mazandaran, Iran, Tel. +98-9149082245; Fax: +98-054-33425737; email: Youse.mahdavi@gmail.com*
[c]*Department of Environmental Engineering, Catholic Kwandong University, 522 Naegok-dong, Gangneung 210-701, Korea, Tel. +82-10-8891-7635; Fax: +82-33-642-7635; email: leesm@cku.ac.kr (S.-M. Lee), Tel. +82-10-5188-4535; email: lhsiama27@gmail.com (Lalhmunsiama)*

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ABSTRACT

In this study, rice straw was crushed into a particle size of 1–2 mm and treated with hydrochloric acid. The changes in surface morphology of rice straw before and after the acid treatment were obtained by SEM images. Moreover, the surface functional groups of rice straw were characterized by FT-IR analysis. The ability of acid treated rice straw to remove 2-chlorophenol (2-CP) from aqueous solution was evaluated in batch adsorption process. The percentage removal of 2-CP using modified rice straw remained almost constant while increasing the pH from 3 to 5 and further increases in the solution pH caused a decrease in the removal of 2-CP from aqueous solutions. The adsorption process was very fast and an apparent equilibrium was attained within 60 min of contact time and the kinetic data fit better to pseudo first-order kinetic model. The equilibrium sorption data were analyzed by Langmuir, Freundlich, Temkin, Dubinin-Radushkevich and Redlich-Peterson isotherm models. Equilibrium data fit well to the Langmuir model and a maximum adsorption capacity was found to be 26.712 mg/g at 20°C. The adsorption capacity increased at higher temperature which indicates that sorption of 2-CP by modified rice straw was endothermic. Free energy of adsorption (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) changes were calculated to predict the nature of adsorption. The estimated values for ΔG° were decreased from –34.726 to –39.472 as the temperature increased from 20 to 60°C, and this result infer that a spontaneous process occurred in the adsorption of 2-CP by modified rice straw. Therefore, this investigation suggests that acid modified rice straw can be employed as an effective and low-cost adsorbent for removal of 2-CP from aqueous solutions.

Keywords: 2-Chlorophenol; Rice straw; Kinetics; Isotherm; Thermodynamic; pH

1. Introduction

In recent decades, a remarkable increase in environmental pollution occurs due to diverse application of various chemicals in industries [1,2]. Chlorophenols are an important chemical which is announced as priority water pollutants by EPA [3]. Chlorophenols are derivatives of phenols, which have one or more chlorine in their structure. Various types of industrial processes such as high-temperature coal conversion, petroleum refining and the manufacture of plastics, resins, textile, iron, steel and paper have significant role in releasing of chlorophenols into aquatic environment [3,4]. Chlorophenols are very toxic, highly soluble in water and stable in the

* Corresponding authors.

environment. An intake to human body may probably cause serious problems such as increasing of respiratory rate, weakness, tremors, seizures and coma. Moreover, they can accumulate in tissues and involves in formation of mutation and cancers [4,5]. Furthermore, previous studies have shown that a very low concentration of chlorophenols (~0.01 mg/L) is able to create unpleasant taste and odor in water [6]. Therefore, the elimination of these compounds from water and wastewater is very important to protect the human health.

Various techniques have been employed for the removal of chlorophenols from water. Due to the simplicity of operation and low cost, the adsorption process has advantages over other techniques in pollutant removal from aqueous solutions [7,8]. Owing to the large specific surface area, well-developed porosity and elegant surface-containing functional groups, activated carbon is widely used for adsorption of phenols and its derivative compounds from aqueous solutions. However, use of activated carbon is not feasible due to the high cost of the commercial activated carbon [9,10]. Recently, many researchers focused on inexpensive and efficient adsorbents as an alternative material to commercial activated carbon [10–12]. Agricultural wastes are widely applied for this proposes and they were found to be suitable potential adsorbents in the removal of phenol and its derivatives compounds [12,13]. Rice is abundantly cultivated in Iran; therefore, rice straw is a one of the largest agricultural by-product in this country. Rice straw is commonly burned after harvesting to prepare the field for the next crop, which in turn releases carbon dioxide (CO_2) as the principal product of the combustion along with carbon monoxide (CO), nitrogen oxides (NO_x) and relatively less amount of sulphur dioxide (SO_2) and methane (CH_4). Moreover, it has been reported that burning of crops residues contribute harmful pollutants in air such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-*p*-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs) which have toxicological behaviour and particularly potential carcinogens [14,15].

Rice straw is one of major lignocellulosic waste that has been used in several studies to remove various type of pollutant; however, the application of rice straw for the removal of phenol derivative compounds is scarce. Several researchers report a significant increase in surface area of materials due to acid treatment which consequently improve the removal efficiency of pollutants from aqueous solutions [16–18]. Moreover, it has been reported that rice straw modified with citric acid and sulphuric acid were successfully utilized for the removal of malachite green and basic dye, respectively [19,20]. So it is assumed that the modification of rice straw using hydrochloric acid possibly will increase the surface area of rice straw and thereby improve its efficacy in the removal of various pollutants from aqueous solutions. Therefore, the aim of the present work is to evaluate the performance of hydrochloric acid treated rice straw for the removal of 2-chlorophenol (2-CP) from aqueous solution. The effect of various parameters such as solution pH, contact time, and initial 2-CP concentration and temperature were investigated. Moreover, the kinetic, isotherm, and thermodynamic modeling were also conducted in this study.

2. Materials and methods

2.1. Preparation of adsorbent

Rice straw was collected from rice paddy in Sari city, Iran. It was then sun dried and crushed into particle sizes in the range of 1–2 mm. The crushed particles were then treated with 0.1 M HCl for 5 h followed by washing with distilled water and then it was kept in a shade until completely dry. The resultant biomass was subsequently used in sorption experiments.

2.2. Characterization of materials

The specific surface area of acid treated rice straw was determined by the BET method using an ASAP 2000 apparatus based on nitrogen adsorption–desorption isotherms at 77 K. The FT-IR analysis was conducted using Nicolet 5,700 instrument, Thermo Corp, USA. The spectra were recorded in the range of 400–4,000 cm^{-1} to find out the information regarding the bending and stretching vibrations of functional groups which are responsible for the adsorption process. The surface morphology of rice straw before and after acid treatment were captured by scanning electron microscopy (SEM) (Philips XL30).

The PZC (point of zero charge) of the modified rice straw was determined by the pH drift method [17]. In brief, 500 mL of distilled water was boiled in erlenmeyer flask for 20 min to expel the dissolved CO_2. The flask was capped with cotton to avoid re-absorption of atmospheric CO_2 by water and cooled at room temperature. Then, 0.01M NaCl solution was prepared from CO_2 free water and 50 ml of this solution was taken out in six different plastic bottles. The pH of solution in each flask were adjusted to pH values of 2, 4, 6, 8, 10 and 12 by adding 0.1M HCl/NaOH solutions. Subsequently, 0.15 g of the modified rice straw was added in each bottles and agitated at 25°C for 24 h. The final pHs of each solution were measured and a graph was plotted between initial pH vs. final pH. The point at which the curve crossed the line pH_{final} equals to $pH_{initial}$ was taken as pH_{PZC} of the material.

2.3. Preparation of 2-CP solution

2-chlorophenol (2-CP) is a phenolic compound with molecular weight of 128.56 g/mol. The structure of 2-CP is shown in Fig. 1. The 2-CP (C_6H_5ClO) used in this work was analytical grade procured from Merck, Germany. For adsorption experiments, the 2-CP solutions with concentrations in the range of 10–200 mg/L were prepared by successive dilution of the stock solution (1,000 mg/L). Deionized water was used for all experiments. All other chemicals used in this study were of analytical grade.

2.4. Batch experiments

The adsorption of 2-chlorophenol using modified rice straw was carried out in batch system. Various experimental conditions which may influence the adsorption of 2-CP including initial solution pH, contact time, initial 2-CP concentration and temperature were tested under batch experiments. In order to determine the effect of the initial solution pH, the experiments was performed within the initial pH of

3–11 with the initial 2-CP concentration of 50 mg/L at 25°C. The effect of contact time was conducted with initial concentrations of 50 mg/L using 5 g/L sorbent at pH 3.0. The flasks were agitated with 180 rpm under constant temperature 30°C. The samples were taken at predetermined time intervals, centrifuged and analyzed for the residual 2-CP concentrations. Moreover, the concentration dependence data were collected between 25–200 mg/L at pH 3.0. Also, the equilibrium sorption data were obtained at various temperatures of between 293 and 333 K. The experiments were performed in a rotary shaker at 180 rpm using 200 mL Erlenmeyer flasks containing a certain amount of modified rice straw in 100 mL of 2-CP solution. After equilibrium, the samples were centrifuged at 3,600 rpm for 10 min and analyzed to determine the residual 2-CP concentrations. A temperature controlled water bath shaker (SHZ-88, Shanghai, China) was used to control the temperature. All pH measurements were carried out using a pH meter (Model pHS-3C, Shanghai, China). The initial pH of the solutions were adjusted to constant values by adding different concentrations (0.01, 0.1, 1.0 M) of HCl or NaOH solutions. The concentrations of 2-CP were measured by a high-performance liquid chromatography (HPLC), Shelton, CT, USA equipped with diode-array detector and a Polaris C18 column. The mobile phase was a mixture of acetonitrile and distilled water in the proportion of 45/55. The HPLC pump was controlled at the flow rate of 1.0 ml/min, and the UV detector was set at 280 nm. The reported concentration for each sample is the average of three separate measurements.

The 2-CP removal efficiency (%), amount of 2-CP sorbed per unit biomass at time t (q_t in mg/g) and at equilibrium (q_e in mg/g) were calculated from Eqs. (1)–(3), respectively [21].

$$R(\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

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

$$q_e = \frac{C_0 - C_e}{m} \times V \quad (3)$$

where C_0 is the 2-CP initial concentration (mg /L), C_t and C_e are the concentrations at time '*t*' and at equilibrium (mg/L), respectively; '*V*' is the volume of the 2-CP solution (*L*); and '*m*' is the weight of adsorbent (g).

3. Results and discussion

3.1. Characterization of material

The specific surface area of adsorbent is one of the most important parameters as the adsorption capacity usually increased with an increase in specific surface area. The BET analysis has shown that the surface area of rice straw was significantly increased after acid treatment and the surface area of unmodified and modified rice straw were found to be 58.5 and 80 m^2/g, respectively. This result suggests that the acid treated rice straw probably possessed higher affinity to remove the pollutants from aqueous media. SEM technique was employed to observe the surface physical morphology of the materials. Fig. 2 shows the SEM micrographs of the modified rice straw before and after the acid treatment. The cavities present on the surface of rice straw were visible from the SEM micrographs. It is clearly to be observed that modified rice straw showed more open pore structure with various size and shapes which may cause to increase an internal surface area of the material.

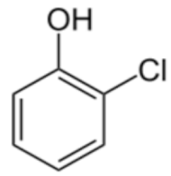

Fig. 1. Structure of 2-chlorophenol (2-CP).

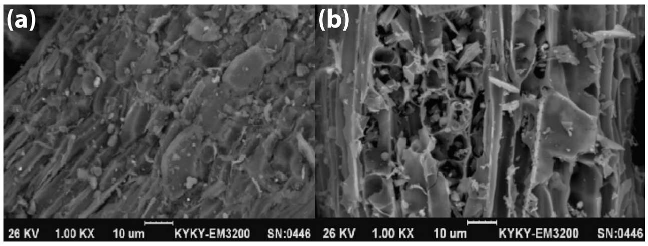

Fig. 2. Scanning electron microscopy image of (a) rice straw (b) modified rice straw.

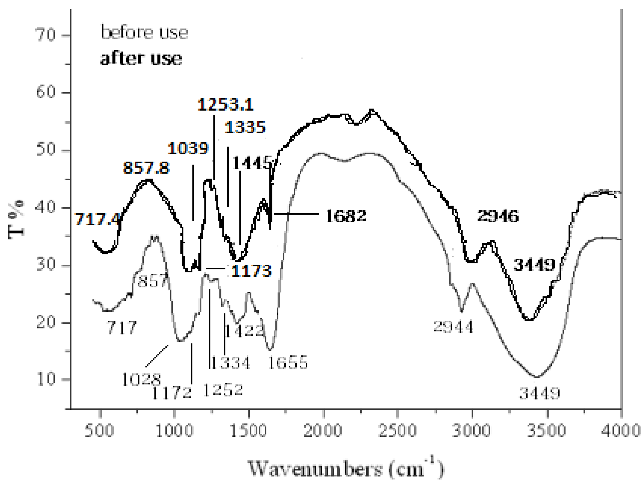

Fig. 3. The FT-IR spectra of modified rice straw before and after adsorption of 2-CP.

In order to investigate the interaction between the functional groups on the surface of rice straw and 2-CP, the modified rice straw were examined before and after adsorption of 2-CP using FT-IR spectroscopy. As shown in Fig. 3, FT-IR spectra obtained before and after the sorption of 2-CP showed a similar pattern. The absorption band obtained at 3,449 cm^{-1} is due to hydroxyl (O-H) group in cellulose and lignin and a small peak obtained at 2,944 cm^{-1} is assigned to the C-H stretching mode [22]. Another intense peak at 1,655 cm^{-1} is due to C=C stretching vibration and distinguish peak at 1,422 cm^{-1} is attributed to C-O stretching vibration of carboxyl group [22,23]. The other peaks obtained between 1,200 and

1,000 cm^{-1} are attributed to C-O group of cellulose, lignin and hemicelluloses [24]. Also, a prominent peak at 1,028 cm^{-1} and a small weak peak obtained at 857 cm^{-1} may corresponds to Si-O stretching and Si-OH bending vibrations indicating the presence of silica in rice straw [22,25]. Furthermore, it is to be observed that the predominant peak obtained at the wave numbers of 1,655 cm^{-1} was significantly reduced after the adsorption of 2-CP and a shift in wave number from 1,422 to 1,445 cm^{-1} and 1,028 to 1,039 cm^{-1} were occurred in the spectra of modified rice straw before and after the adsorption of 2-CP. These results indicate the reasonable amount of 2-CP were adsorbed onto the modified rice straw and the shift in wavenumbers suggest that carboxyl group were largely involved in the removal of 2-CP using modified rice straw [26,27].

3.2. Batch experiments

3.2.1. Effect of pH

The pH of a solution is an important parameter affecting the adsorption process as it affects both speciation of the adsorbate and the surface binding site of the sorbent [28]. Fig. 4 shows that the uptake of 2-CP by the modified rice straw was almost constant in the pH range of 3–5. However, the adsorption of 2-CP decreased abruptly when the pH value exceeds 5.0. The large reduction in 2-CP removal at pH higher than 5.0 was attributed to ionic repulsion between deprotonated 2-CP molecules and negatively charged surface of the adsorbents. The pKa value of 2-CP is 8.56 which suggests that 2-CP predominantly remain in undissociate neutral phenol and start to dissociate above pH 8.56 and form phenoxide ion. Moreover, the pH_{pzc} of the modified rice straw was found to be ~5.0. At lower pH ($pH < pH_{zpc}$), the adsorbent surface carries net positive charge while the adsorbent surface charge is negative at the pH higher than the pH_{pzc} ($pH > pH_{zpc}$). Therefore, it is assumed that the undissociated species of 2-CP is preferred by the positively charge surface of the adsorbents and result in higher percentage removal at lower pH [21]. Besides, 2-CP possibly will dissociate into phenoxide form at higher pH value which eventually cause to reduced the removal of 2-CP from aqueous solutions due to the electrostatic repulsion between the negatively charged of the adsorbent and adsorbate species [6]. An earlier report also has shown that the removal efficiencies of 2-chlorophenol, 3-chlorophenol and 4-chlorophenol by coir pitch carbon, rice straw carbon and rattan sawdust activated carbon, respectively, were found to be higher at lower pH values and decreases with increasing the solution pH [6,14,18].

3.2.2. Adsorption kinetics

Adsorption kinetic of 2-CP onto modified rice straw and unmodified rice straw were investigated by measuring the amount of 2-CP removed at various interval of time. As shown in Fig. 5, the percentage adsorption increased rapidly at the beginning and the apparent equilibrium time for the adsorption of 2-CP using modified and unmodified rice straw were found to be 60 and 90 min, respectively. In addition, Fig. 5 showed that the percentage removal of 2-CP using modified rice straw was significantly higher than that of unmodified rice straw. In this experimental condition, a pseudo-first order kinetic model has shown the maximum uptake of 2-CP by rice straw and modified rice straw were 7.773 and 9.792 mg/g, respectively.

The kinetic data obtained at various initial concentrations of 2-CP were analyzed using pseudo-first-order (PFO), pseudo-second-order (PSO) and intra particle diffusion models. The kinetic models were used in non-linear form and the pseudo-first-order-kinetic model was taken as:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (4)$$

where q_t is the amount of adsorbate removed at time t (mg/g); q_e is the maximum uptake at equilibrium (mg/g), k_1 and t are the pseudo-first order rate constant (1/min) and the contact time (min), respectively [17]. Moreover, the pseudo-second order kinetic rate equation was utilized as:

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

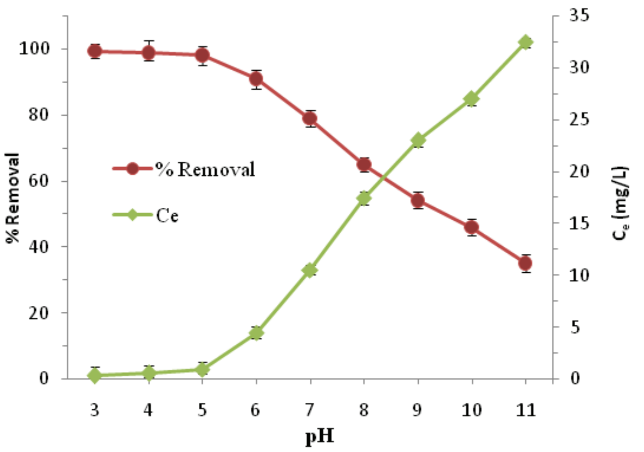

Fig. 4. Effect of pH on the removal of 2-CP using modified rice straw (dosage = 6 g/L, C_0 = 50 mg/L, T = 298 K, and Contact time = 90 min).

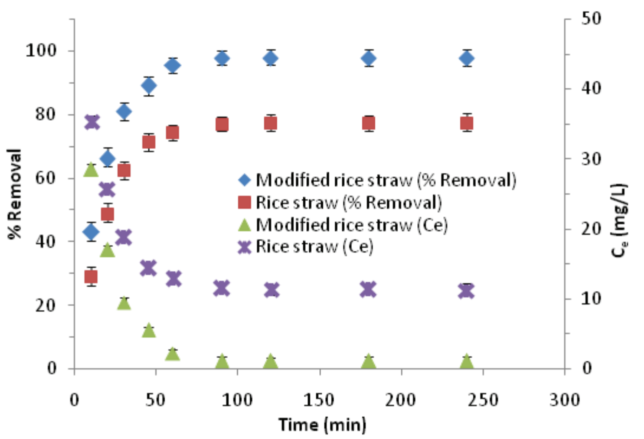

Fig. 5. Percenage removal of 2-CP at various contact time using unmodified and modified rice straw (dosage = 5 g/L, C_0 = 50 mg/L, pH = 3.0, T = 303 K).

where q_e is the amount of 2-CP removed at equilibrium (mg/g) for; q_t is the amount of 2-CP removed at time t (mg/g); and k_2 is the pseudo-second-order kinetic constant rate (g/mg·min) [29]. The non-linear plots of pseudo-first order and pseudo-second order kinetic model for the removal of 2-CP using modified rice straw at various concentrations are shown in Figs. 6 and 7, respectively.

The kinetic data collected at four different concentrations fit well to non-linear pseudo-first order kinetic as the least square sum (s^2) obtained from pseudo first-order kinetic model were found to be lower than that obtained for pseudo second-order kinetic model. The rate constants and maximum amount of 2-CP removed were calculated for the two kinetic models and given in Table 1. Although the least square sum obtained for the second-order kinetic model obtained at various concentration are relatively low, the calculated q_e values are comparatively higher than the values obtained from the pseudo first-order kinetic model. The calculated values of q_e (q_e, cal) obtained from the pseudo first-order model perfectly agreed with the experimental values of q_e (q_e, exp). Therefore, the results revealed that the non-linear pseudo first-order kinetic model is best for describing the adsorption kinetics of 2-CP onto modified rice straw.

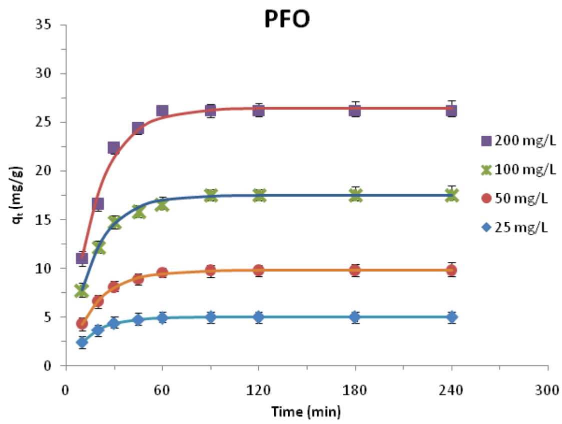

Fig. 6. Non-linear plot of pseudo-first-order kinetic for the removal of 2-CP using modified rice straw (dosage = 5 g/L, C_0 = 25–200 mg/L, pH = 3.0, T = 303 K).

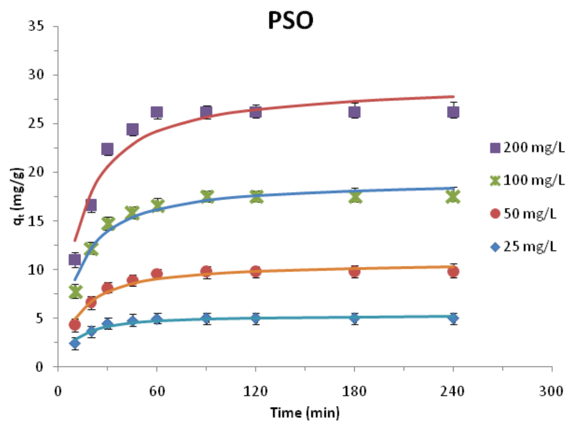

Fig. 7. Non-linear plot of pseudo-second-order kinetic for the removal of 2-CP using modified rice straw (dosage = 5 g/L, C_0 = 25–200 mg/L, pH = 3.0, T = 303 K).

The adsorbate transport from the solution to the surface of the adsorbent occurs in several steps. This phenomenon may be controlled by one or more steps such as film or external diffusion, pore diffusion, surface diffusion and adsorption on the pore surface, or a combination of more than one step through the adsorption process [30,31]. Therefore, the time dependent intra-particle diffusion of 2-CP from the surface adsorption site to the interior site of modified rice straw was analyzed by intra-particle diffusion model as given in Eq. (6). The intra-particle diffusion equation was taken as:

$$q_t = k_{\text{dif}} t^{\frac{1}{2}} + C \quad (6)$$

where k_{dif} is the intra-particle diffusion rate constant (mg/g·min) and C is the intercept. The value of C relates to the thickness of the boundary layer. The larger C implies the greater effect of the boundary layer [32]. If the plot of q_t vs. $t^{0.5}$ gives a straight line and pass through the origin, the adsorption process is controlled by intraparticle diffusion only. However if the data exhibit multi-linear plots, two or more steps must be involved in the sorption process. The value C in Eq. (6) is a constant that gives an idea about the thickness of the boundary layer [33]. The intra-particle diffusion plot for the removal of 2-CP using modified rice straw is shown in Fig. 8. From this figure, it can be observed that three consecutive steps were involved in the adsorption of 2-CP by modified rice straw. The first linear section is attributed to the surface adsorption which is also called external surface adsorption. The second linear section describes the gradual adsorption with intra-particle diffusion as a rate limiting steps and the third section corresponds to the final equilibrium stage where adsorption becomes very slow and stable, and finally attained the adsorption equilibrium [34].

Table 1
Kinetic parameters for the adsorption of 2-CP using modified rice straw at various concentration

Conc. (mg/L)	$q_{e,\text{exp}}$	Pseudo first order kinetic			Pseudo second order kinetic		
		k_1 (1/min)	q_e (mg/g)	s^2	k_2 (g/mg/min)	q_e (mg/g)	s^2
25	4.972 ± 0.068	0.067 ± 0.004	4.984 ± 0.062	0.008	0.019 ± 0.004	5.423 ± 0.052	0.422
50	9.783 ± 0.097	0.056 ± 0.003	9.792 ± 0.093	0.039	0.007 ± 0.003	10.792 ± 0.115	1.422
100	17.652 ± 0.128	0.058 ± 0.003	17.491 ± 0.124	0.527	0.004 ± 0.003	19.284 ± 0.132	3.647
200	26.284 ± 0.192	0.054 ± 0.002	26.472 ± 0.182	2.917	0.002 ± 0.002	29.263 ± 0.195	19.517

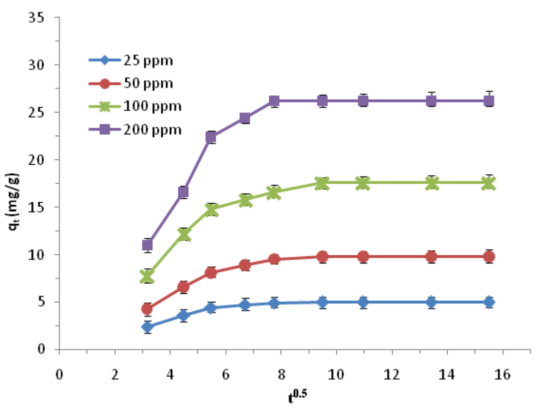

Fig. 8. Intra-particle diffusion plot for adsorption of 2-CP onto modified rice straw (dosage = 5 g/L, C_0 = 25–200 mg/L, pH = 3.0, T = 303 K).

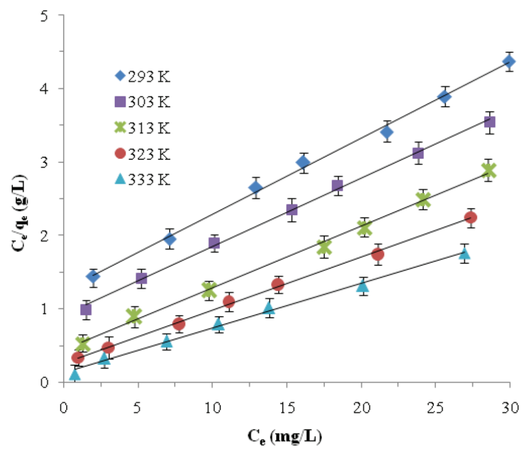

Fig. 9. Langmuir adsorption isotherm of 2-CP removal using modified rice straw at various temperatures (dosage = 6 g/L, C_0 = 25–200 mg/L, pH = 3.0, T = 293–333 K, contact time= 120 min).

3.2.3. Adsorption isotherms

Adsorption isotherm is basically important to describe the nature of the adsorbents as well as the interaction between the solutes and the adsorbents [35]. The Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm models were used to describe the relationship between the amount of phenol adsorbed and its equilibrium concentration in solutions.

The equilibrium adsorption data obtained at various concentrations were evaluated by the following isotherm models. The Langmuir isotherm is valid for monolayer adsorption on a surface containing a finite number of identical sites. The model assumes uniform adsorption on the surface and no transmigration of adsorbate in the plane of the surface [36]. The linear form of the Langmuir adsorption isotherm was taken as [37]:

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

where C_e (mg/L) is the equilibrium concentration of the adsorbate; q_e (mg/g) is the amount of 2-CP adsorbed per unit mass of adsorbent; q_m is the maximum monolayer adsorption capacity (mg/g) and K_L is Langmuir constant related to rate of adsorption.

Fig. 9 shows a linear relationship of C_e/q_e vs. C_e using experimental data obtained, suggesting the suitable applicability of the Langmuir model ($R^2 \geq 0.997$). The good fitting of the model suggests monolayer coverage of modified rice straw by 2-CP is significant at the outer surface of the adsorbent. Values of q_m and K_L were calculated from the plot of C_e/q_e vs. C_e and the values obtained are given in Table 2. A dimensionless constant separation factor (R_L) of Langmuir isotherm (Eq. (8)) was used to determine the favorability of the adsorption process [38]. The value of R_L indicates the type of the isotherm which maybe either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

$$R_L = \frac{1}{1 + K_L C_0} \quad (8)$$

K_L is the Langmuir constant and C_0 is the initial 2-CP concentration (mg/L). The R_L values obtained at various temperatures were given in Table 2. The fractional values obtained at all the five different temperature indicate that the adsorption of 2-CP using the modified rice straw is a favorable process.

The concentration dependence sorption data were analyzed with Freundlich adsorption isotherm. The Freundlich equation is based on the hypothesis of multi-layer adsorption. The linear equation was utilized as follows [37]:

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

where K_F and $1/n$ are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively. Generally, the adsorption capacity of an adsorbent for a given adsorbate enhances with an increase in K_F.

Temkin considered the effects of indirect adsorbate-adsorbent interactions on adsorption isotherms. The heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbate-adsorbate interactions. Temkin isotherm in its linear form was taken as [35]:

$$q_e = B \ln A + B \ln C_e \quad (10)$$

where $B = RT/b$, T is the absolute temperature in Kelvin and R is the universal gas constant (8.314 J/mol·K). A is the equilibrium binding constant and 'b' corresponds to the heat of sorption.

Moreover, Dubinin-Radushkevich model, a more generalized model compared to the Langmuir isotherm was used for analyzing the concentration dependence data. This model is based on the fact that there is no homogeneous surface or constant adsorption potential. The linear form of (D–R) isotherm model was taken as [39]:

$$\ln q_e = \ln q_m - K\varepsilon^2 \quad (11)$$

where K is a constant corresponding to the biosorption energy; q_m is the theoretical saturation capacity and ε is

Table 2
Adsorption isotherm constants for the removal of 2-CP using modified rice straw at different temperatures

Isotherm models	20°C	30°C	40°C	50°C	60°C
Langmuir					
q_m (mg/g)	26.712 ± 0.125	26.943 ± 0.132	27.456 ± 0.132	28.348 ± 0.153	29.853 ± 0.144
K_L (L/mg)	0.087 ± 0.004	0.102 ± 0.003	0.195 ± 0.004	0.277 ± 0.003	0.475 ± 0.002
R_L	0.213	0.325	0.642	0.562	0.784
R^2	0.997	0.998	0.999	0.998	0.999
Freundlich					
K_F (mg/g)	3.053 ± 0.081	3.267 ± 0.092	3.474 ± 0.064	3.786 ± 0.072	4.184 ± 0.053
n	5.076 ± 0.022	3.745 ± 0.025	3.003 ± 0.046	2.347 ± 0.033	1.845 ± 0.037
R^2	0.863	0.852	0.871	0.894	0.914
Temkin					
A (L/g)	1.505 ± 0.008	1.218 ± 0.007	0.846 ± 0.007	0.566 ± 0.006	0.293 ± 0.005
B	9.266 ± 0.054	12.146 ± 0.065	13.297 ± 0.074	15.684 ± 0.071	19.146 ± 0.093
R^2	0.821	0.845	0.794	0.807	0.825
D-Radushkevich					
q_m (mg/g)	22.102 ± 0.112	22.423 ± 0.102	23.125 ± 0.121	23.596 ± 0.135	24.616 ± 0.136
K.10^{-4} (mol^2/ K·J^2)	2.145 ± 0.021	1.663 ± 0.009	1.096 ± 0.008	0.946 ± 0.008	0.563 ± 0.006
E (kJ/mol)	0.512 ± 0.005	0.586 ± 0.006	0.645 ± 0.006	0.714 ± 0.005	0.859 ± 0.007
R^2	0.894	0.912	0.935	0.906	0.889
R–Peterson					
k_R (L/mg)	45.205 ± 0.172	39.305 ± 0.157	37.646 ± 0.168	29.178 ± 0.145	26.425 ± 0.137
aR (L/mg)	0.074 ± 0.004	0.045 ± 0.003	0.257 ± 0.004	0.424 ± 0.005	0.672 ± 0.006
B	0.645 ± 0.005	0.711 ± 0.004	0.825 ± 0.007	0.886 ± 0.006	0.912 ± 0.007
R^2	0.795	0.831	0.804	0.776	0.845

the Polanyi potential which was calculated by below equation:

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

where R (kJ mol^{-1} K^{-1}) is the gas constant and T (K) is the absolute temperature. Mean adsorption energy (E) was calculated from the K value by the following relation:

$$E = \frac{1}{(2K)^{\frac{1}{2}}} \quad (13)$$

Redlich and Peterson (R-P) have proposed an empirical equation incorporating three parameters which may be used to represent adsorption equilibrium over a wide concentration range, and can be applied either in homogeneous or heterogeneous systems due to its versatility. Therefore, the linear form of Redlich and Peterson isotherm model was taken as:

$$\ln\left(\frac{k_R C_e}{q_e}-1\right) = \ln a_R + \beta \ln C_e \quad (14)$$

where k_R(L/g) and a_R (L/mg) are the R–P constants; β is the exponent which has a value between 0 and 1 and C_e the equilibrium liquid phase concentration (mg/L) [40].

The results and correlation coefficients are presented in Table 2. By comparing the correlation coefficients (R^2), it can be seen that the experimental equilibrium sorption data were best described by the Langmuir model. The values of R_L were found within the range of 0.216–0.784 and this again confirmed that the adsorption of 2-CP onto the rice straw was favorable under the specified experimental conditions in this study. This result suggests a monolayer coverage of the surface of modified rice straw by 2-CP [41]. Moreover, it was observed that the sorption capacity ($q_{\max}$) and the K_F increase with increases in temperature. The maximum sorption capacity of various adsorbents along with modified rice straw as determined by Langmuir adsorption isotherm are given Table 3. It is obvious from Table 3 that the modified rice straw possessed reasonably high sorption capacity for the removal of 2-CP from aqueous solutions.

3.2.4. Thermodynamic analyses

To estimate the effect of temperature on the adsorption of 2-CP onto modified rice straw, the extent of 2-CP removal was evaluated at temperature of 293, 303, 313, 323, 333 K and the enthalpy change (ΔH°) and entropy change (ΔS°) were determined using the Van't Hoff equation (Eq. (15)):

$$\ln K_D = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \quad (15)$$

Table 3
Langmuir sorption capacity of 2-CP obtained for various adsorbents along with modified rice straw

Adsorbent	Adsorption capacity (mg/g)	Refs.
Seed of *Adenopus breviflorus*	13.43	[42]
Azolla Filiculoides biomass	7.8	[43]
Rice straw derived ash	37.0	[44]
Carbonaceous adsorbent	50.3	[45]
Blast furnace sludge	20.4	[45]
Blast furnace dust	14.0	[45]
Modified rice straw	26.71	Present study

Table 4
Thermodynamic parameters obtained for adsorption of 2-CP onto modified rice straw (Initial 2-CP concentration: 100 mg/L; pH: 3.0 and contact time: 120 min)

Tem (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
293	–34.726	34.885	118.641
303	–35.913		
313	–37.099		
323	–38.285		
333	–39.472		

where K_D is the equillibrium constant obtained by taking the ratio of maximum uptake of 2-CP by modified rice straw (q_e) and the equilibrium concentration (C_e) of 2-CP, R is the universal gas constant (8.314 J/mol·K) and T is the temperature (K) [46,47]. The values of ΔH° and ΔS° are determined from the slope and intercept of the van't Hoff plots of ln K_L vs. 1/T and found to be 34.885 kJ/mol and 118.641 J/mol·K, respectively. It was suggested that the ΔH° value for physisorption is smaller than 40 kJ/mol; therefore, the ΔH° value obtained suggests that the adsorption of 2-CP onto rice straw occurred through physisorption process. The value of ΔH° was positive which indicates that the adsorption reaction was endothermic [48]. The positive value of ΔS° reflects the affinityof rice straw for 2-CP and suggests an increased in randomness at the interface of solid and solution during the adsorption process. Furthermore, the free energy change (ΔG°) for the adsorption of 2-CP onto modified straw at various temperatures were calculated using the following equation (Eq. (16)):

$$\Delta G° = \Delta H° - T\Delta S° \quad (16)$$

The thermodynamic parameters obtained at various temperatures are given in Table 4. The values of ΔG° were found to decrease from –34.726 to –39.472 kJ/mol while increasing the reaction temperatures from 293 to 333 K. The negative values confirm the feasibility of the process and the spontaneous nature of the adsorption. The decrease in the negative value of ΔG° with an increase in temperature indicates that the adsorption of 2-CP on rice straw was more favorable at higher temperatures [49].

4. Conclusions

The adsorption of 2-CP from aqueous solution using modified rice straw was investigated under various experimental conditions in batch method. The percentage removal of 2-CP using rice straw remained almost constant while increasing the pH from 3.0 to 5.0 and further increases in the solution pH caused a decrease in the removal of 2-CP from aqueous solutions. The adsorption process was very fast and an apparent equilibrium was attained within 60 min of contact time and the pseudo first-order kinetic model best described the adsorption process. The equilibrium sorption data were analyzed by Langmuir, Freundlich, Temkin, Dubinin-Radushkevich and Redlich-Peterson isotherm models. Equilibrium data fit well to the Langmuir model and a maximum adsorption capacity was found to be 26.712 mg/g at 20°C. The adsorption capacity was found to increase with increasing temperature which indicates that sorption of 2-CP by modified rice straw was endothermic. Free energy of adsorption (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) changes were calculated to predict the nature of adsorption. The estimated values for ΔG° were found to decreased from -34.726 to –39.472 kJ/mol as the temperature increased from 273 to 333 K, and this result infers that a spontaneous process occurred in the adsorption of 2-CP by modified rice straw. Moreover, ΔH° value obtained indicates that the adsorption of 2-CP onto modified rice straw occurred via a physisorption process. Therefore, this study demonstrated that modified rice straw is an effective and potential adsorbent for the removal of 2-CP from aqueous solutions.

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