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Adsorption of Orange II dye from aqueous solutions using phosphoric-acid modified clam shell powder

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ABSTRACT

In this study, the clam shell, a waste biomaterial, was modified with phosphoric acid to improve the adsorption amount of Orange II dye. The effects of initial concentration, contact time, and temperature on the adsorption were studied. The equilibrium adsorption data of Orange II on the phosphoric acid-modified clam shell powder (PCSP) were adequately represented by Langmuir isotherm with an adsorption capacity of 1,017.13 mg/g, which is higher than that obtained using raw clam shell powder. Adsorption kinetics followed the pseudo-second-order rate expression. Thermodynamic parameters show that the process is exothermal, feasible, and spontaneous. The effect of temperature inferred that the type of adsorption in the study is a physical adsorption. Therefore, PCSP is an efficient and economical adsorbent for dye removal.

Keywords: Adsorption; Orange II; Clam shell; Wastewater treatment; Dye

1. Introduction

Dyes are usually present in the effluent water of several industries, including textiles, leather, paper, printing, and cosmetics. Humans have used dyes since the dawn of civilization [1]. Today, nearly 40,000 dyes and pigments are listed, which consists of over 7,000 different chemical structures [2]. The complex aromatic structures of synthetic dyes make them more stable and more difficult to remove from the effluents discharged into the water bodies [3]. Therefore, dye removal is an important and challenging area of wastewater treatment because some dyes and their degradation products may be carcinogenic and toxic to animals.

Several methods have been employed in removing dyes, such as physical, chemical, and biological processes, to treat wastewaters contaminated with organic pollutants and dyes. The most commonly used methods for color removal are biological oxidation and chemical precipitation. However, these processes are only effective and economical when the solute concentrations are relatively high. The adsorption technique is an efficient and economical way of removing dyes, even from dilute solutions, and in controlling the biochemical oxygen demand [4–7]. The adsorption characteristics of dyes on various adsorbents have been extensively investigated for separation and purification. However, the information on the adsorption capacities of most adsorbents are still limited [8]. New, economical, easily available, and highly effective

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adsorbents are still under continuous development. Therefore, this study aims to develop an inexpensive adsorbent for wastewater treatment using clam shell powder.

Clam shell is the hard protective outer layer of certain marine animals. In most cases, it is the exoskeleton of an invertebrate, an animal without a backbone. The shell is usually made of outer layers of proteins, followed by an intermediate layer of calcite, and then a smooth inner layer of platy calcium carbonate crystals [9]. Clam shell is an easily available natural material commonly found in beaches. Clams are also common seafood in several countries, wherein the clam shell is often thrown away. Some studies investigated the application of shell powder as low-cost adsorbent [10,11]. However, the adsorption amounts are very low, indicating that shell powder is not suitable for industrial application.

Further studies are needed to improve the adsorption of low-cost adsorbents. This study modified the clam shell powder with acid treatment using H_3PO_4. After the modification, more micropores are produced and the chemical properties of the surface changed.

This study aims to investigate and explore the possibility of using phosphoric acid-modified clam shell powder (PCSP) for Orange II adsorption from aqueous solutions. This study reports, for the first time, the feasibility of applying PCSP as low-cost alternative adsorbent for the removal of Orange II from aqueous solutions. The effects of adsorbent dose, initial dye concentration, contact time, and temperature on dye adsorption using PCSP were investigated. Adsorption kinetics, isotherms, and thermodynamic parameters were also evaluated and reported.

2. Methods

2.1. Materials

The Orange II dye ($C_{16}H_{11}N_2NaO_4S{\cdot}5H_2O$, molecular weight of 350.32) was used as the target adsorbate in the study. The dye was purchased from the National Pharmaceutical Group Chemical Reagent Co., Ltd. (China) and used without further purification.

The raw clam shells were obtained from the commercial market in Changzhou City (Jiangsu, China). The samples were cleaned with tap water to remove fresh remnants attached to the shells and then dried at 100℃ for 2 h. The shells were crushed, ground and passed through a 100-mesh sieve.

The modification process included the following steps: (1) The clam shell powder was added in the phosphoric acid solution (3%) with a ratio of 1:20 (weight). (2) The powder was immersed in the acid solution for 6 h. (3) The pH of the acid solution was adjusted to 8 using ammonia solution. (4) The clam shell powder was allowed to age for 3 h and then (5) washed with deionized water several times. (6) Lastly, the powder was dried at 105℃ for 2 h. The resulting PCSP was stored in the desiccator prior to the physical and adsorption characterization.

2.2. Methods

For equilibrium measurements, a known amount of the PCSP was added into a set of 22 mL centrifuge tubes containing a known amount of Orange II dye. The concentrations ranged from 80 mg/L to 3,000 mg/L. The tubes were capped and placed on a digital heating circulating water bath for 6 h to ensure apparent equilibrium. In the experiment on the effect of temperature on adsorption, temperature was held at 286, 293, and 306 K. Preliminary kinetic investigations revealed that the adsorption equilibrium was reached in less than 6 h. Therefore, the batch tests of adsorption lasted for 10 h. When equilibrium was attained, the adsorbent was separated by centrifugation at 2,500 rpm for 10 min. Afterward, the supernatant was analyzed for residual concentration using a Shimadzu UV-2450 Spectrophotometer with a wavelength of 485 nm. This procedure was used in all batch adsorption experiments in the study. The amount of adsorbed Orange II at equilibrium, q_e (mg/g), was calculated using the following equation:

$$q_e = V(C_0 - C_e)/W \tag{1}$$

Where C_0 and C_e (mg/L) are the liquid-phase concentrations of dye at initial and at equilibrium, respectively; V (L) is the volume of the solution; and W (g) is the mass of adsorbent used.

The procedures of kinetic experiments were identical with the other equilibrium tests. The effect of contact time on the amount of adsorbed dye was investigated with 400 mg/L initial concentration of dye at 25℃. The amount of dye adsorbed by PCSP at time, t, was calculated from the concentrations in the solution before and after adsorption. The amount of Orange II adsorbed by PCSP, q_t (mg/g), was calculated from the mass balance equation:

$$q_t = V(C_0 - C_t)/W \tag{2}$$

Where q_t (mg/g) is the amount of dye adsorbed by the modified PCSP at time, t; C_0 and C_t (mg/L) are the respective initial and liquid-phase concentrations of Orange II at time, t; V (L) is the volume of Orange

II solution, and *W* (g) is the mass of PCSP sample used.

2.3. Characterization

The specific surface area was determined from the nitrogen adsorption data using the BET method. Nitrogen adsorption/desorption isotherm was measured at -196°C using Autosorb-1 (Quantachrome, USA). The sample was degassed overnight at 200°C prior to the adsorption measurements.

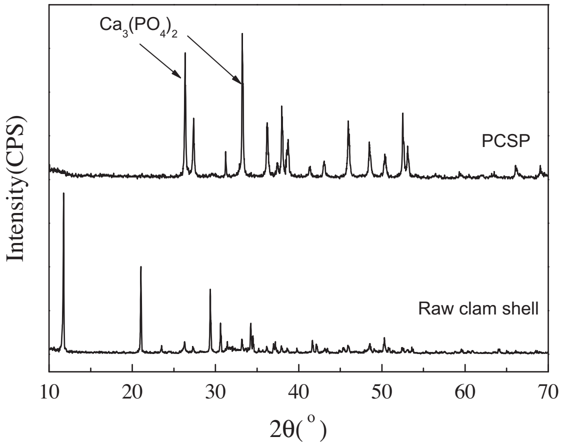

Fig. 1. XRD pattern of the raw clam shell and PCSP.

The X-ray diffraction (XRD) patterns of the prepared samples were acquired with an X-ray diffractometer (Max-2550PC, Rigaku D) using Cu K_α radiation (40 kV, 300 mA) with a wavelength of 0.154 nm to confirm the structure of the materials. All XRD patterns were obtained from 0.5° to 70°, with a scan speed of 4°/min.

High-resolution transmission electron microscopy (TEM) was performed using a JEOL JEM-2100 LaB6 Transmission Electron Microscope (Japan).

Fourier transform infrared (FTIR) spectra were obtained using the KBr-pressed-disk technique on a Thermo Nicolet Nexus 670 FTIR spectrophotometer. The FTIR spectra from 4,000 to 400 cm^{-1} were recorded with a resolution of 4 cm^{-1}. After the recording, 64 interferograms were collected.

3. Results and discussion

3.1. Characterization

Fig. 1 shows the XRD patterns of the raw clam shell and PCSP, wherein a significant difference existed between the two samples. In addition to the common reflections observed in the diffraction

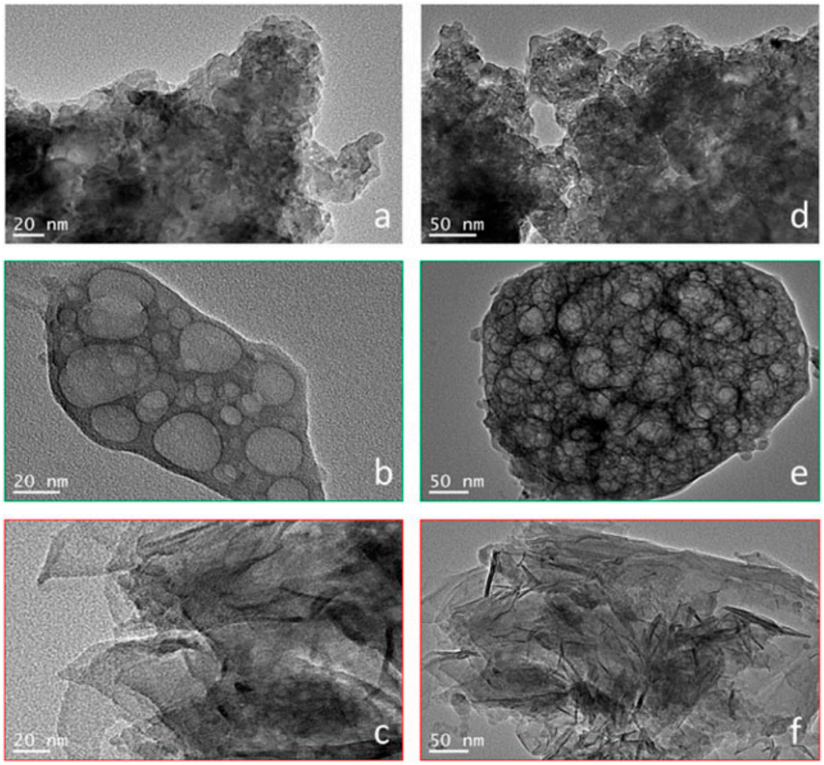

Fig. 2. TEM micrographs of the raw clam shell (a, d), PCSP (b, e), and Orange II adsorbed on PCSP (c, f).

patterns of the samples corresponding to quartz and mullite crystalline phases, the peaks assigned to calcium phosphate were identified in the XRD pattern of the PCSP sample. The results showed that the clam shell modification using H_3PO_4 caused the formation of surface moieties containing phosphorus and calcium. These moieties are expected to increase the adsorption properties of the modified clam shell via surface adsorption.

The TEM photos in Figure 2 show the existence of several pores and cavities on the PCSP surface. The pores that covered the surface of the shell powder had a diameter of about 20 nm. The specific surface area increased from 2.6 to 16.0 m^2/g after modification. Calcium phosphate is formed when calcium carbonate, the main component of the shell, reacts with phosphoric acid. The phosphoric acid erodes the surface of the shell and more micropores appear at the surface.

In Fig. 3, the FTIR spectra of raw clam shell, PCSP, Orange II, and PCSP with adsorbed Orange II were recorded from 400 to 4,000 cm^{-1} for comparison.

The absorption peaks from 3,400 to 3,650 cm^{-1} are due to the H–O–H stretching vibrations of water molecules and the –OH stretching vibrations of adsorbed water. The strong bands in the raw clam shell at 860.8 and 1479.7 cm^{-1} corresponds to the v2-symmetric bending and v3-asymmetric stretching, respectively, which are characteristics of the calcite structure. After modification with phosphoric acid, the adsorption bands at 1058.8 and 1134.5 cm^{-1} are assigned to the P–O$^-$ groups comprising the phosphate non-bridging oxygen portion of the PO_4 tetrahedra in the chain structure [12,13]. The peaks of Orange II at 1,619.7 and 1,507.7 cm^{-1} are assigned to the aromatic C=C stretching vibration. The weak peak at 1,034.7 cm^{-1} corresponds to the –N=N– bond stretching vibration and the peak at 1,209.1 cm^{-1} is assigned to the –C–O– bond stretching vibration. The –SO_3– asymmetric vibrations is shown at 1,121.9 cm^{-1} [14]. The peaks of the adsorbed Orange II by PCSP were similar to those adsorbed by raw clam shell, but with a slight shift, indicating that the type of adsorption in the experiment was a physical adsorption.

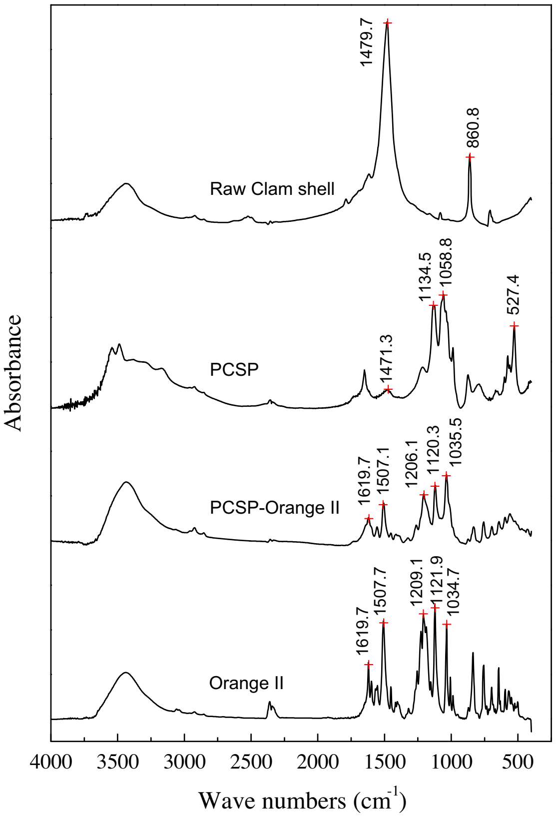

Fig. 3. FTIR spectra for the raw clam shell, PCSP, Orange II, and adsorbed Orange II.

3.2. Adsorption isotherms

The adsorption equilibrium isotherm is important in describing the distribution of adsorbate molecules (PCSP) between the liquid and the solid phases when the adsorption of Orange II reaches an equilibrium state. The adsorption amounts increased linearly with the increase in equilibrium concentration when the equilibrium concentration is below 600 mg/L, as shown in Figure 4. The R^2 of the linear fitting for PCSP and raw clam shell powder are 0.92 and 0.95, respectively. The slopes of the two fitted lines are 10.5 and 0.17, respectively. The adsorption of Orange II extremely improved because of the modification made on the raw clam shells. The pH values of the solution were analyzed. The pH of the Orange II solution

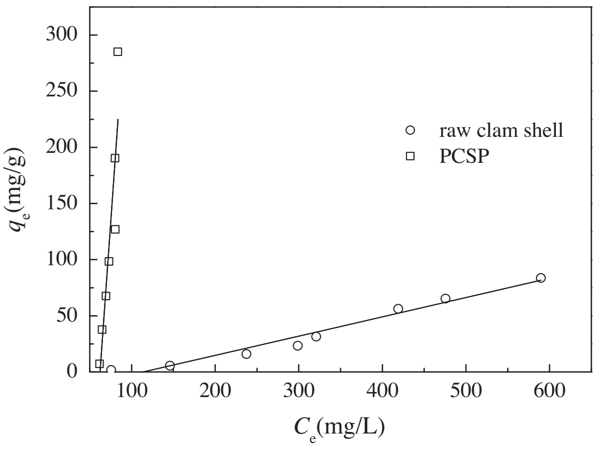

Fig. 4. Comparison on the adsorption of Orange II on raw clam shell and PCSP (dosage: 1.5 mg/mL).

before adsorption is about 5.9. After adsorption, the increased pH values are from 6.7 to 6.9. The result indicates that calcium carbonate, the main ingredient of the shell, can adjust the pH value of wastewater to neutral.

The adsorption of Orange II on PCSP was investigated at various temperatures (286, 293 and 306 K). The results are fitted to the Langmuir and Freundlich models, as shown in Figure 5. The adsorption capacity increased sharply as it approaches the equilibrium concentration. Moreover, temperature significantly affected the adsorption, indicating that absorption is dependent on temperature.

The Langmuir model assumes that there is no interaction between the adsorbate molecules and the adsorption is localized in a monolayer. The Langmuir isotherm [15] is represented by the following equation:

$$q_t/Q_0 = bC_e/(1 + bC_e) \tag{3}$$

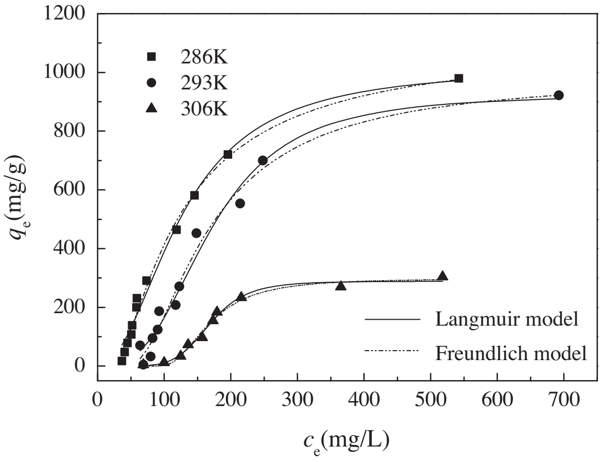

Fig. 5. Isotherms of Orange II adsorbed on PCSP at various temperatures (dosage: 1.5 mg/mL).

Where C_e (mg/L) is the equilibrium concentration, q_e (mg/g) is the amount of adsorbed adsorbate per unit mass of adsorbate at equilibrium, Q_0 (mg/g) is the maximum amount of adsorbed adsobate per unit mass of adsorbate, and b is the Langmuir constant that is related to adsorption capacity. All parameters were calculated from this isotherm, and the values are listed in Table 1. The adsorption capacity is about 1017.13 mg/g at 286 K, which is much higher than previous reports. In a previous study [10], the highest adsorption capacity of Basic Green 4 on sea shell is only 42.331 mg/g, whereas the other study showed that the adsorption capacity of an Oyster shell is only 0.084 mg/g[11]. Although the specific surface area was not very high compared with some regular adsorbents, the adsorption capacity is much higher than those in previous reports.

Furthermore, the effect of the isotherm shape can predict whether an adsorption system is favorable or unfavorable. The separation factor or equilibrium parameter ($R_{L)}$, another important parameter, is expressed in this study as [16]:

$$R_L = 1/(1 + bC_0) \tag{4}$$

Where b is the Langmuir constant and C_0 (mg/L) is the highest dye concentration. The value of R_L indicates whether the isotherm is unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$). The R_L values for Orange II adsorption onto PCSP were less than 1 and greater than zero, indicating a favorable adsorption (Table 1).

The Freundlich isotherm model is an empirical relationship that describes the adsorption of solutes from a liquid to a solid surface and assumes that different sites with several adsorption energies are involved. The Freundlich equation [17] is expressed as follows:

Table 1
Langmuir and Freundlich constants for the adsorption of Orange II

Isotherms	Parameters	Temperatures (K)		
		286	293	306
Langmuir	Q_0, mg/g	1,017.13	925.66	284.53
	b, $\times 10^{-5}$ L/mg	3.99	3.47×10^{-2}	2.61×10^{-9}
	r_L^2	0.988	0.978	0.981
	R_L	0.999	0.999	0.893
Freundlich	K_F, (mg/g) (L/mg)$^{1/n}$	1,110.02	984.93	297.33
	N	13.3	13.1	8.2
	r_F^2	0.983	0.982	0.947

$$q_e = K_F C_e^{1/n} \tag{5}$$

Where q_e is the amount adsorbed at equilibrium (mg/g) and C_e is the equilibrium concentration of the Orange II. K_F and n are Freundlich constants, where n indicates the degree of which an adsorption process is favorable and K_F (mg/g(L/mg)$^{1/n}$) is the adsorption capacity of the adsorbent. The value of n from 2 to 10 represents good, 1 to 2 means moderately difficult, and less than 1 represents poor adsorption characteristics.

PCSP is a good adsorbent for Orange II ($n > 2$). The $1/n$ ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, wherein the surface is more heterogeneous as its value gets closer to 0 [18]. Accordingly, Freundlich constants (K_F and n) were calculated and listed in Table 1.

The parameters, r_L^2 and r_F^2, are the correlation coefficients of the Langmuir and Freundlich models, respectively. Their values are listed in Table 1. The r_L^2 is closer to 1 than that of r_F^2, indicating that this isotherm was more fitted in the Langmuir model.

As implied by the Langmuir model, the Orange II molecules are adsorbed in monolayer. However, the space for the adsorbate is not adequate because the surface of the PCSP is limited. Some flocculation was observed during adsorption. A more detailed research is required to study the adsorption mechanism in PCSP.

3.3. Kinetic analyses

The prediction on the rate at which contamination is removed from aqueous solutions is important in the design of an adsorption treatment plant. Fig. 6 shows the effect of contact time in the adsorption of Orange II by PCSP. The 90 min adsorption capacity is 114.2 mg/g. The adsorption is initially rapid (contact time < 75 min) and then slows down. This behavior is attributed to the large number of vacant surface sites available for adsorption during the initial stage. Afterward, the remaining vacant surface sites were difficult to occupy because of the repulsive forces between the dye molecules on the PCSP at the bulk phase [19].

Kinetic analysis was conducted using pseudo-first-order and pseudo-second-order models to investigate the adsorption process of Orange II dyes on PCSP. These two models are commonly used to describe the sorption of dyes and other pollutants (heavy metals) on solid sorbents.

The Lagergren rate equation is one of the most widely used adsorption rate equations for the adsorption of solute from a liquid solution. The pseudo-first-order kinetic model of Lagergren [20] may be represented as follows:

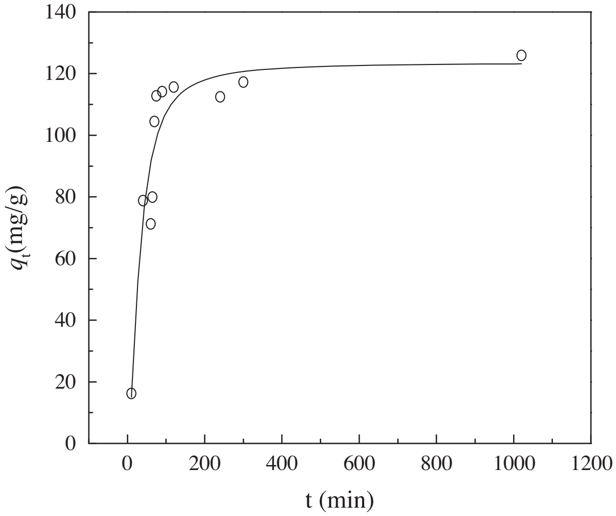

Fig. 6. Effect of contact time on the adsorption of Orange II on PCSP (dosage: 1.5 mg/mL).

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{6}$$

Where q_e and q_t (mg/g) are the respective amounts of Orange II adsorbed at equilibrium and at time t (min), and k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}). Integrating this equation for the boundary conditions, $t = 0$ to $t = t$ and $q = 0$ to $q = q_t$ gives

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \tag{7}$$

A linear plot of $\ln(q_e - q_t)$ vs. t checks the validity of the model. However, the correlation coefficient (r^2) was less than 0.89, indicating that the pseudo-first-order model is not the best-fit model of the data.

The pseudo-second-order equation based on adsorption equilibrium capacity can be expressed as [21]

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{8}$$

where q_e and q_t are the respective amounts of Orange II adsorbed (mg/g) at equilibrium and at time t (min), and k_2 is the rate constant of pseudo-second-order adsorption (g mg^{-1}min^{-1}). Integrating this equation for the boundary conditions, $t = 0$ to $t = t$ and $q = 0$ to $q = q_t$ gives

$$\frac{1}{q_{\mathrm{e}} - q_t} = \frac{1}{q_{\mathrm{e}}} + k_2 t \tag{9}$$

Rearranging the Eq. (7) into linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_{\mathrm{e}}^2} + \frac{t}{q_{\mathrm{e}}} \tag{10}$$

A linear plot of t/q_t vs. t checks the validity of the model (Fig. 7). The rate constant of pseudo-second-order adsorption is determined from the slope of the plot. The values of k_2 and q_{e} are 3.47×10^{-4} g mg^{-1}min^{-1} and 128.37 mg/g, respectively. The linear plot of t/q_t vs. t shows good agreement between the experimental (q_{e}(exp) 125.87 mg/g) and calculated (q_{e}(cal)) values. Furthermore, the correlation coefficient for the second-order kinetics model (r^2) is 0.994, indicating that the rates of adsorption conformed to the pseudo-second-order kinetics with good correlation.

3.4. Thermodynamic analyses

The Gibbs free energy changes ($\Delta G°$), enthalpy changes ($\Delta H°$), and entropy changes ($\Delta S°$) were determined to estimate the effect of temperature on the adsorption of Orange II on PCSP. The effect of temperature on adsorption capacity was investigated by measuring the adsorption isotherms at temperatures of 286, 293, and 306 K. The $\Delta G°$ values were calculated using Eq. (9), whereas the $\Delta H°$ and $\Delta S°$ values were determined from the slope and the intercept of the Van't Hoff plots of $\ln(K_{\mathrm{L}})$ vs. $1/T$ (Eq. (10)). Table 2 presents the thermodynamic parameters at various temperatures.

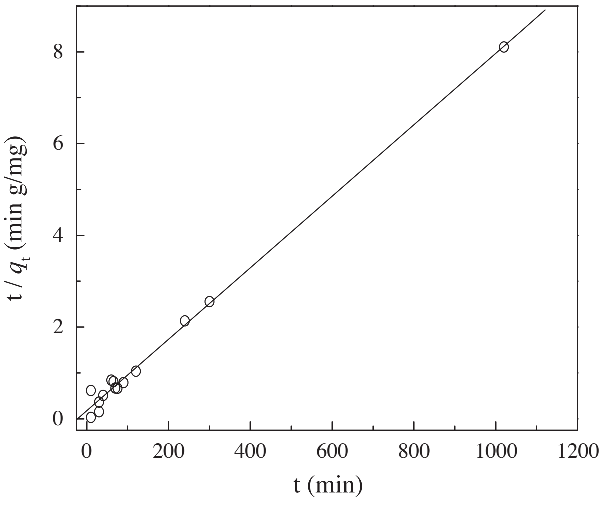

Fig. 7. Plots of pseudo-second-order kinetic model for the adsorption of Orange II on PCSP.

Table 2
Thermodynamic parameter values for the adsorption of Orange II

T (K)	K_{L}	$\Delta G°$ (kJ/mol)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (kJ/mol K)
286	1.81	−3.29	−15.56	−0.042
293	1.33	−3.03		
306	1.12	−2.44		

$$\Delta G^{\circ} = -RT\ln(K_{\mathrm{L}}) \tag{11}$$

$$\ln K_{\mathrm{L}} = -\frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R} \tag{12}$$

Where K_{L} is the Langmuir equilibrium constant (l/mol), R is the gas constant (8.314 J/mol K), and T is the temperature (K).

The K_{L} value is calculated from the following equation [22,23]:

$$K_{\mathrm{L}} = a_{\mathrm{s}}/a_{\mathrm{e}} = v_{\mathrm{e}}q_{\mathrm{e}}/v_{\mathrm{e}}C_{\mathrm{e}} \tag{13}$$

Where a_{s} is the activity of adsorbed sorbate, a_{e} is the activity of sorbate in solution at equilibrium, v_{s} is the activity coefficient of adsorbed sorbate, and v_{e} is the activity coefficient of sorbate in the solution at equilibrium.

The value of K_{L} can be directly calculated using adsorption equilibrium experimental data, where q_e is the amount of dye (mg) adsorbed on the adsorbent per liter of the solution at equilibrium, and C_e is the equilibrium concentration (mg/L) of the dye in the solution. In the dilute range of the solution, the ratio of the activity coefficients was assumed unity. The activity coefficient v approaches unity as the concentration of sorbate in the solution decreases as it approaches zero. Therefore, Eq. (11) can be reduced to the following form:

$$\lim_{q_{\mathrm{e}} \to \max} \frac{a_{\mathrm{s}}}{a_{\mathrm{e}}} = \frac{q_{\mathrm{e}}}{C_{\mathrm{e}}} = K_{\mathrm{L}} \tag{14}$$

The negative values confirm the feasibility of the process and the spontaneous nature of the adsorption. The values of $\Delta G°$ increased from −3.29 to −2.44 kJ/mol using the equilibrium constant, K_{L}. The increase of $\Delta G°$ with the increase in temperature indicates that the adsorption process of Orange II on PCSP becomes more favorable at lower temperatures. The values of $\Delta H°$ and $\Delta S°$ calculated from the plot, $\ln(K_{\mathrm{L}})$ vs. $1/T$, were −15.56 kJ/mol and −0.042 kJ/(mol K), respectively. Kara et al. [24] suggested that the process is

Table 3
Comparison on Orange II adsorption capacity of PCSP with other reported low-cost adsorbents

Adsorbent	$q_{\max}$ (mg g^{-1})	Ref.
Titania aerogels	420	[25]
Rice husk/$MnFe_2O_4$ composite	69.4	[26]
Rice husk/CoFe2O4 composite	65	[26]
Rice husk ash	59.1	[26]
Sludge	270	[27]
Activated carbon fibers	405	[27]
Activated carbon	0.73	[28]
Biosolid sample	0.6	[28]
Hydrotalcite	176.8	[29]
Zeolite	0.63	[30]
2% Cetylpyridinium bromide Hexadecyl (CPB)-modified zeolite	3.62	[30]
2% Hexadecylammonium bromide (HDTMA)-modified zeolite	3.38	[30]
Bentonite with HDTMA	868.1	[31]
Spent brewery grains	30.5	[32]
Chitosan bead	1940	[32]
Chitosan fiber	1,226–1,678	[33]
ODTMA-palygorskite (200% CEC equivalent modification)	99.01	[34]
Clam shell	1017.13	Present study

considered physisorption when the ΔH° values are less than 40 kJ/mol. The value of ΔH° in this study suggests that the adsorption of Orange II on PCSP was a physisorption process. The negative value of ΔH° (−15.56 kJ/mol) indicates that the adsorption reaction was exothermic. The negative value of ΔS° (−0.042 kJ/mol K) reflects the decrease in the disorder of the system at the solid-solution interface and no significant change occurred in the internal structure of the adsorbent during the adsorption process.

The effect of temperature inferred that the type of adsorption in the study is a physical adsorption. The mechanism of the physical adsorption is controlled by the Van der Waals forces existing between the adsorbate and adsorbent. The molecules of Orange II are attracted to the surface of PCSP because of the Van der Waals force. The phosphate eroded the surface of the shell powder and increased its adsorption capacity.

3.5. Comparison of PCSP with other sorbents

Table 3 summarizes the comparison of the maximum Orange II adsorption capacities of various adsorbents including PCSP. The comparison shows that PCSP has higher adsorption capacity of Orange II than the other adsorbents. The easy availability and cost-effectiveness of PCSP are some of the additional advantages, which reflect a promising future for PCSP utilization in Orange II removal from aqueous solutions [25–34].

4. Conclusion

The study showed that the adsorption properties of PCSP can be significantly improved for the removal of Orange II using H_3PO_4 treatment. The amount of adsorbed dye varied with initial solution concentration, contact time, and temperature. The equilibrium adsorption data of Orange II on PCSP were adequately represented by the Langmuir isotherm with an adsorption capacity of 1017.13 mg/g, which is higher than the other adsorbents. The adsorption kinetics followed the pseudo-second-order rate expression. Moreover, the thermodynamic parameters showed that the process is exothermic, feasible, and spontaneous.

Acknowledgments

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