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Research Article

Removal of Azo Dyes (Violet B and Violet 5R) from Aqueous Solution Using New Activated Carbon Developed from Orange Peel

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Activated carbon developed from agricultural waste orange peel (COP) was prepared. COP was characterized using Fourier infrared spectroscopy (FTIR), X-ray powder diffraction (XRD), scanning electron microscopy (SEM), and BET. COP has surface area and mean pore diameter of 225.6 m² g⁻¹ and 22.40 nm, respectively. The removal of violet B (VB) and violet 5R (V5R) from aqueous solutions by COP was investigated. The effect of operational parameters such as contact time, pH, initial dye concentration, and adsorbent dosage on the adsorption of dyes was investigated. Maximum dye was removed within 30 min of contact time at pH > 7. Two common models, the Langmuir and Freundlich isotherms, were used to investigate the interaction of dye and COPs. The isotherm evaluations revealed that the Langmuir model provides better fit to the experimental data than the Freundlich model. The adsorption of VB and V5R onto COP was followed by pseudo-second-order kinetic model with a good correlation ($R^2 > 0.99$). Activation energies 5.47 and 29.7 KJ mol⁻¹ were determined for violet B and violet 5R, respectively. The rate of adsorption of violet 5R was faster than that of violet B ($k_{V5R} > k_{VB}$). The prepared COP could thus be used as promising adsorbent for removal of organic dyes, especially azo dye, from polluted water. The solid COP could be conveniently regenerated after adsorption.

1. Introduction

Many industries employ dyes and pigments to color their products. Most dyes are inert and nontoxic at the concentration discharged into the receiving water. Dyes are usually stable to photodegradation, biodegradation, and oxidizing agents [1]. Color removal from effluents is a major environmental problem because of difficulty of treating such streams by conventional physicochemical and biological treatment methods [2]. Many physical and chemical methods such as coagulation, precipitation, and oxidation have been used for dye removal from water [3]. Adsorption has been described in order to eliminate or lower concentration of a wide range of dissolved pollutants (organic or inorganic) in the effluent [4]. Dye removal by different sorbents was evaluated [5, 6]. Activated carbon is the most widely used adsorbent for this purpose. It has high capacity for adsorption of organic maters,

but its uses are limited, because of its high cost [7, 8]. This has led to search for cheaper sorbents such as mineral clays [9–12], sawdust [13–16], and so on. Recently, various kinds of activated carbon have been achieved from different agriculture wastes and used as low-cost sorbents for removal of heavy metals, organic compounds, and dyes from aqueous solution [17–20]. Orange, as a kind of biological resources, is available in large quantities in many parts of the world. The orange peel mainly consists of cellulose, hemicellulose, and lignin in the form of carboxyl and hydroxyl. Since the orange peel is available free of cost from orange processing industries, only the carbonization of it is involved for the waste for wastewater treatment would not only be economical but also will help to solve solid waste disposal problems [21–24].

The main objective of this work is possibility of using activated carbon from orange peels as a low-cost adsorbent for removal of violet B and violet 5R from aqueous solutions.

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FIGURE 1: Chemical structure of (a) violet B and (b) violet 5R.

The effects of important experimental parameters such as contact time, initial dye concentration, adsorbent concentration, and ionic strength were studied. The adsorption kinetics and isotherms were described.

2. Experimental

2.1. Material and Method. Orange peels were collected from a local fruit field in the south of Iran. The collected biomaterial was extensively washed under tap water to remove any particulate sprayed with distilled water (OP). Then, they were dried in oven at 100°C for 24 h and were sieved. After sieving the particle size of materials was remained between 1 and 5 mm

Violet B (VB) and violet 5R (V5R) were obtained from Merck. The stock solution of $1000 \, \text{mg} \, \text{L}^{-1}$ of VB and V5R was prepared. The dilution was done in water when necessary. All chemicals were analytical grade reagents from Merck and were used without any purification.

2.2. Preparation of the Adsorbent or COP. Activated carbon from orange peel was prepared. The orange peel sample biomass $500.0\,\mathrm{g}$ was added in small portion to $1.0\,\mathrm{L}$ of 98% $\mathrm{H_2SO_4}$ during 6 h and resulting reaction mixture was cut into small pieces. They were air-dried in an oven at $100-120\,^{\circ}\mathrm{C}$ for $24\,\mathrm{h}$. Activated carbons were carried out in a muffle furnace. A crucible was cleaned and heated to a constant weight. The orange paste was then transferred into the crucible and latter was placed in the furnace. The orange paste was activated at $700\,^{\circ}\mathrm{C}$ ($5\,^{\circ}\mathrm{C/min}$) for $3\,\mathrm{h}$. The activated product was cooled down to room temperature, washed with distilled water, and then dried in the oven at $100\,^{\circ}\mathrm{C}$ for $6\,\mathrm{h}$ [24].

2.3. Adsorbate Preparation. 1-Naphthalenesulfonic acid, 3- $((4'-((2-amino-8-hydroxy-6-sulfo-1-naphthalenyl)azo)(1,1'-biphenyl)-4-yl)azo)-4-hydroxy-, disodium salt (violet B) and 5-(Acetylamino)-4-hydroxy-3-[[2-hydroxy-4-[[2-(sulfooxy)ethyl]sulfonyl]phenyl]azo]-2,7-naphthalenedisulfonic acid trisodium salt (violet 5R) as pollutant models were used. Violet B is double azo class with molecular formula of <math>C_{32}H_{21}N_5Na_2O_8S_2$ (MW = 713.65). Violet 5R is mono azo

class with molecular formula of $C_{20}H_{16}N_3O_{15}S_4Na_3$ (MW = 735.58).

A stock solution of 1000 mg L^{-1} of each dye was prepared in double distilled water. It is subsequently whenever necessary diluted. Chemical structure of violet B and violet 5R is shown in Figure 1.

Adsorption studies were carried out in glass vessels with agitation provided by a shaker. The temperature was controlled at 25°C by air bath. The suspensions containing 0.1 g COP and varying amounts of dyes were shaken on an orbital shaker at 150 rpm. Samples for the kinetic study were taken at different time intervals. For adsorption experiments, 50 mL dye solution (50–150 mg L $^{-1}$) and 0.1 g of COP were used. The effect of pH was studied by adjusting of pH of the solutions in the range of 2–12 with 0.1 N NaOH or HCl solutions. Samples were withdrawn at appropriate time intervals and centrifuged at 3000 rpm for 5 min and the absorbance of the supernatant was measured using a UV-vis spectrophotometer (Shimadzu 160-A, Japan) at $\lambda_{\rm max}$ of each dye. The results are average as at least 3 experiments.

Kinetics of adsorption was determined by analyzing sorptive uptake of the dye from aqueous solution at different time intervals. For sorption isotherms determination, dye solutions of different concentrations were agitated with known amount of sorbents till the equilibrium was achieved at room temperature (25°C).

IR measurements were performed by FTIR tensor-27 of Burker Co. Pressed pellets were prepared by grinding the powder specimens with spectroscopic grade KBr for FTIR spectra test. All pH measurements were carried out with an ISTEK-720P pH meter. Scanning electron microscopy was performed using a Philips SEM model XL30 electron microscope. The powder X-ray diffraction studies were made on Philips PW3719 X-ray diffractometer by using Cu-K $_{\alpha}$ radiation of wave length 1.54060 Å. The specific surface area was measured by N $_2$ adsorption-desorption isotherm and was obtained with an ASAP 2010 instrument (Micromeritics).

The percent removal of violet B and violet 5R by the hereby adsorbent is given by

$$\%\text{Removal} = \frac{C_0 - C_e}{C_0 \times 100},\tag{1}$$

g)	Mean pore diameter (nm)	Total pore volume (cm ³ g ⁻¹)	Surface area (m ² g ⁻¹)
	13.56	6.92	22.4

14.5

TABLE 1: Characterization of OP and COP.

22.40

where C_0 , C_e denotes the initial and equilibrium dye concentration (mg L⁻¹). The amount of dye adsorbed (q_e) was determined by using the following equation:

Sample weight (g

0.1920

0.1915

$$q_e = \frac{\left(C_0 - C_e\right)V}{m},\tag{2}$$

where V is the volume of the solutions (mL) and m is the amount (mg) of adsorbent.

3. Results and Discussion

Sample

OP

COP

3.1. Characterization of Adsorbent. FTIR spectra of OP, COP and activated carbon (Merck) are shown in Figure 2. In OP spectrum (Figure 2(a)) the broad and intense adsorption peaks at around 3400 cm⁻¹ correspond to O-H stretching vibrations due to inter and inter-molecular hydrogen banding of polymeric compounds (macromolecular associations), such as alcohols, phenols and carboxylic acids, as in pectin, cellulose groups on the adsorbent surface. The peaks at 2924 cm⁻¹ are attributed to the symmetric and asymmetric C-H stretching vibration of aliphatic acids. The peak observed at 1751 cm⁻¹ is the stretching vibration of bond due to nonionic carboxyl groups (-COOH, -COOCH₃) and may be assigned to carboxylic acids or their esters. Peaks at 1000-1080 cm⁻¹ may be due to stretching vibration of C-OH of alcoholic groups and carboxylic acids. The peak observed at 1618 cm⁻¹ is due to C=C stretching that can be attributed to the aromatic C-C bond. The peaks observed at 623 cm⁻¹ correspond to the C-C group [25]. Figure 2(b) shows that the prepared activated carbon from orange peel. It shows the functional groups of surface of orange peel disappeared. Figure 2(c) shows the activated carbon from Merck. Comparing Figures 2(b) and 2(c) confirmed the activated carbon from orange peel.

The FTIR spectra of COP and dye loaded COP was illustrated in Figures 2(d) and 2(e), in order to compare the differences among them with COP. From Figures 2(d) and 2(e), the broad bonds at 3400–3600 cm⁻¹ and 3300–3450 cm⁻¹ correspond to O–H stretching vibrations of violet 5R loaded COP and violet B loaded COP, respectively. The appearance of bonds at 1000–2200 in Figures 2(d) and 2(e) also shows the presence of dye on the surface of COP. From the results, presence of functional groups of dyes was observed at FTIR of them and COP acts as a good sorbent.

SEM image of COP before and after adsorption of VB shows in Figure 3. The SEM image is shown the porous nature of COP. The COP has cylindrical porous shape and homogeneous distribution with mean pore diameter 22.40 nm. The COP particles have surface area of 225.6 m² g⁻¹ and total pore volume 14.5 cm³ g⁻¹ (Table 1). After adsorption of dye, a significant change was observed in structure of surface of

carbon orange peels. The peels appear to have a rough surface because they are covered by dye molecules.

X-ray diffraction patterns for activated carbon and COP are shown in Figure 4. The positions of the peaks due to d_{002} and d_{100} reflections are attributed to $2\theta=25.1^{\circ}$ and 45° , respectively [26]. These diffraction peaks are evidence that the samples have a turbostratic structure. This turbostratic model assumes that the sample is made of graphite-like microcrystallites, bounded by cross linking network, consisting of several graphite-like layers, stacked nearly parallel and equidistant, with each layer having a random orientation. The value of d_{002} is comparable with those reported by Kumar et al. on activated carbon cloth [27].

3.2. Effect of Contact Time. Equilibrium time is important parameter for wastewater treatment process. The relation between removal of violet B and violet 5R and reaction time were studied. Figure 5 shows the percentage removal of violet B and violet 5R on comparison with activated carbon from Merck at different contact times. The adsorption increases with increasing of contact time. Obviously, the adsorption equilibrium was attained after stirring for 60 min. It was found that more than 70% removal of violet B and 75% removal of violet 5R occurred in the first 30 min of contact time, and thereafter the rate of adsorption was found to be slow. The rapid adsorption at the initial contact time is due to the availability of the porosity surface of COP adsorbent which led to fast adsorption of dyes. Therefore, the fast adsorption rate reflects good accessibility of the binding sites of the COP for violet B and violet 5R. This has practical advantages in terms of reducing reactor volumes and time. The later slow rate of adsorption has probably occurred due to the slow pore diffusion of the solute ion into the bulk of the adsorbent. The equilibrium was found to be nearly 60 min when the maximum dye adsorption capacity was reached. Therefore, the adsorption time was fixed at 60 min in subsequent adsorption experiments. The results also showed that the COP can act as activated carbon for removal of dyes.

3.3. Effect of pH on Violet B and Violet 5R Uptake. The pH of the system is very effective on the adsorption capacity of adsorbate molecule presumably due to its influence on the surface properties of the adsorbent and ionization/dissociation of the adsorbate molecule. Figure 6 shows the effect of pH on the removal of violet B and violet 5R from aqueous solution by COP. Effect of pH on adsorption of violet B and violet 5R onto COP ($100 \, \text{mg L}^{-1}$) was done at room temperature ($25 \pm 2\,^{\circ}\text{C}$), agitation speed $150 \, \text{rpm}$ for the minimum contact time required to reach the equilibrium ($60 \, \text{min}$). With increasing in pH from 2 to 6, the percent of dye removal increased from 69 to 90% and from 65 to 86% for V5R and VB, respectively.

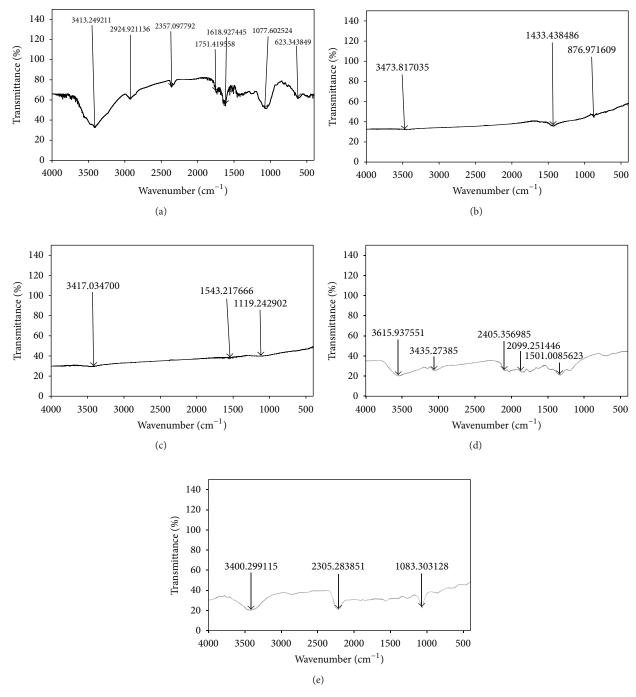


FIGURE 2: FTIR spectra of (a) OP, (b) COP, (c) activated carbon (Merck), (d) violet 5R loaded COP, and (e) violet B loaded COP.

However, two possible mechanisms of adsorption of dyes on COP adsorbent may be considered: (a) electrostatic interaction between the adsorbent and dye and (b) the chemical reaction between the dye and the adsorbent.

Low pH value (2.0–6.0) leads to an increase in H^+ ion concentration in the system and the surface of the COP acquires positive charge by absorbing H^+ ions (3). On the other hand, at low pH, H^+ may compete with dye ions for adsorption sites of COP, thereby inhibiting the adsorption

of dyes. As the COP surface is positively charged at low pH value, a significantly strong electrostatic repulsion appears between the sorbent surface and dye molecule leading to minimum adsorption of dyes. On the other hand, increase of the pH value (basic condition) led to increase of the number of negatively charged sites and the number of positively charged sites decreases as in (4). A negatively charged surface site on the COP dose is favoring adsorption of dye molecules due to the electrostatic attraction (5). The lowest adsorption

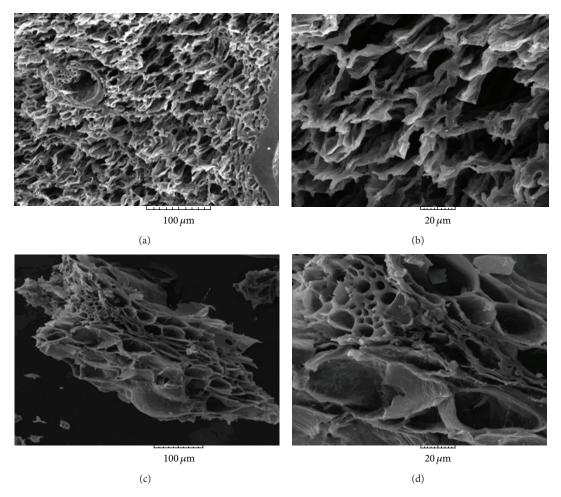


FIGURE 3: SEM image of COP (a), (b) before and (c), (d) after adsorption of VB.

occurred at pH 2.0 and the greatest adsorption occurred at pH > 7.0. Therefore, optimum pH value > 7.0 for dye adsorption was determined [28, 33]

$$R-OH + H^{+} \rightleftharpoons R-OH_{2}^{+}$$
 (3)

$$R-OH + OH^{-} \rightleftharpoons R-O^{-} + H_{2}O \tag{4}$$

$$R-O^- + dye^+ \rightleftharpoons R-O-dye$$
 (5)

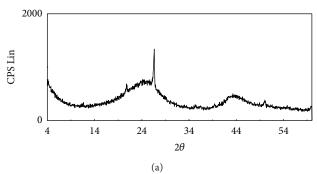
From results of pH study and (3), (4), and (5), it seems that the mechanisms of adsorption were done by electrostatic interaction between COP and dyes.

3.4. Effect of Initial Dyes Concentration. The experimental results of the sorption of violet B and violet 5R on COP at various initial dye concentrations are investigated. The experiments were carried out at adsorbate doses $0.4\,\mathrm{g}/50\,\mathrm{mL}$ in the test solution, room temperature $(25\pm2^\circ\mathrm{C})$ at different initial concentrations of violet B and violet 5R $(50, 75, 100, 125\,\mathrm{and}\,150\,\mathrm{mg}\,\mathrm{L}^{-1})$ for $60\,\mathrm{min}$. The percentage of adsorption efficiency was decreased with increasing of initial dye concentration in the solution [24]. However, the percentage removal of dye was greater at lower initial concentrations and smaller at higher initial concentrations. In the process of violet dyes

adsorption initially dye molecules have to first encounter the boundary layer effect and then it has to diffuse from boundary layer film onto adsorbent surface and then finally it has to diffuse into the porous structure of the adsorbent. This phenomenon will take relatively longer contact time. These results clearly indicate that the adsorption of violet B and violet 5R from its aqueous solution was dependent on its initial concentration.

3.5. Effect of Adsorbent Mass on Dye Adsorption. The adsorption of violet B and violet 5R on COP was studied by changing the mass of adsorbent (0.05–2.0 g/50 mL) in the test solution at initial violet B and violet 5R concentration (100 mg L $^{-1}$), temperature (25 ± 2°C), and alkaline pH at contact time for 60 min (Figure 7). The percent of adsorption was increased and equilibrium time was decreased when adsorbent doses increased. The adsorption increased rapidly, when COP dose was increased from 0.05 to 0.5 g/50 mL at equilibrium time 60. This can be attributed to increasing of surface area of COP and availability of more adsorption sites [34].

3.6. *Isotherm Data Analysis.* Adsorption is usually described through an isotherm. The adsorption isotherm indicates how the adsorbed molecules distribute between the liquid phase



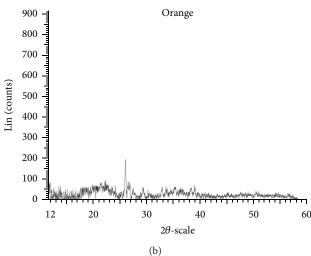


FIGURE 4: XRD patterns of (a) activated carbon and (b) COP.

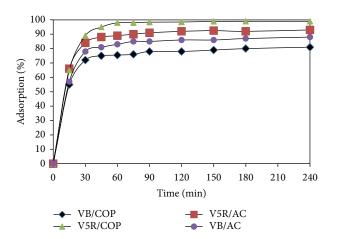


FIGURE 5: Effect of contact time on the removal of violet B and violet 5R onto COP.

and the solid phase when the adsorption process reaches an equilibrium state. Several models describe the adsorption process. The experimental data for COP adsorbing violet B and violet 5R could be fit by Langmuir and Freundlich isothermal models. The Langmuir model is in the linear form:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{\text{max}}} + \frac{C_e}{q_{\text{max}}},\tag{6}$$

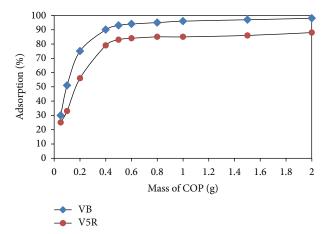


FIGURE 6: Effect of pH on adsorption of violet B and violet 5R onto COP (100 mg L^{-1}) at room temperature.

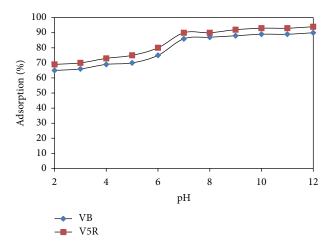


Figure 7: Effect of adsorbent mass on adsorption of violet B and violet 5R (50 mL of $100~{\rm mg\,L}^{-1}$) onto COP.

where $q_{\rm max}$ (mg g⁻¹) represents the maximum amount of dye per unit weight of adsorbent to form a complete monolayer on the surface, K_L is the equilibrium adsorption constant, q_e is the amount of dye adsorbed by adsorbent at equilibrium, and C_e is the equilibrium concentration of dyes. The linearized Freundlich model is

$$\ln q_e = \ln k + \frac{1}{n} \ln C_e, \tag{7}$$

where 1/n represents Freundlich intensity parameter and K_F indicates the adsorption capacity of COP. Langmuir equation and Freundlich equation were fitted to the isotherm data as shown in Table 2. Langmuir isotherm shows better fitting model with higher correlation coefficient ($R^2 > 0.98$) compared to Freundlich isotherm ($R^2 < 0.950$). The high correlation coefficient of Langmuir isotherm indicates that dyes strongly adsorbed to the surface of COP. It is verified that COP has great potential to be a good adsorbent for the removal of dye in water treatment. Table 2 shows the Langmuir and Freundlich isotherm parameters for violet B and

Campla	Freundlich		Langmuir			
Sample	K_F	n	R^2	$q_{ m max}~({ m mgg^{-1}})$	$K_L (\mathrm{Lmg^{-1}})$	R^2
Violet B						
$50 \mathrm{mg}\mathrm{L}^{-1}$	4.366	0.86	0.935	38.6	33.65	0.980
100mg L^{-1}	4.47	0.91	0.862	42.5	35.32	0.975
150 mg L^{-1}	4.83	0.94	0.944	44.2	36.7	0.986
Violet 5R						
50 mg L^{-1}	5.26	0.78	0.940	36.45	42.0	0.992
$100 \mathrm{mg} \mathrm{L}^{-1}$	5.34	0.82	0.880	36.96	43.4	0.995
$150 \mathrm{mg} \mathrm{L}^{-1}$	5.41	0.86	0.924	37.26	44.2	0.996

TABLE 2: Langmuir and Freundlich isotherm parameters for violet B and violet 5R adsorption onto COP.

violet 5R adsorption onto COP. The results showed that the maximum adsorption capacity of COP was increased by increasing of adsorbent dosage from 0.1 to 1.0 g. For violet B maximum adsorption capacity of COP was increased from 38.6 mg g⁻¹ to 49.2 mg g⁻¹ and for violet 5R from 52.45 mg g⁻¹ to 87.26 mg g⁻¹, respectively.

3.7. Adsorption Kinetics. The kinetic parameters give important information for designing and modeling of adsorption processes. Thus, pseudo-first-order [35] and pseudo-second-order [36] kinetic models were studied for adsorption of violet B and violet 5R onto COP. The conformity between experimental data and the model-predicted values was expressed by the correlation coefficients (\mathbb{R}^2 , values close or equal to 1, the relatively higher value is the more applicable model).

3.7.1. Pseudo-First-Order Equation. The adsorption kinetic data were described by the Lagergren pseudo-first-order model [35], which is the earliest known equation describing the adsorption rate based on the adsorption capacity. The Lagergren equation is commonly expresses as follows:

$$\frac{dq_t}{dt} = k_1 \left(q_e - q_t \right),\tag{8}$$

where q_e and q_t are the adsorption capacity at equilibrium and at time t, respectively (mg g⁻¹), and k_1 is the rate constant of pseudo-first order adsorption (L min⁻¹).

Integrating (8) for the boundary conditions t = 0 - t and $q_t = 0 - q_t$ and rearranging to obtain the following linear form gives the following equation:

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

Plot of values of $\log(q_e - q_t)$ versus t to give a linear relationship from which k_1 and q_e can be determined from the slope and intercept, respectively (Figure 8).

3.7.2. Pseudo-Second-Order Equation. The adsorption kinetic may be described by the pseudo-second-order model [36], which is generally given as follows

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2,\tag{10}$$

where k_2 (g mg⁻¹ min⁻¹) is the second-order rate constant of adsorption. Integrating (10) for the boundary conditions $q_t = 0$ to $q_t = q_t$ at t = 0 to t = t is simplified as can be rearranged and linearized to obtain the following equation:

$$\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \frac{t}{q_e}.$$
 (11)

It was mentioned that the curve fitting plot of $\log (q_e - q_t)$ versus t does not show good results for the entire sorption period (Figure 8), while the plot of t/q_t versus t gives a straight line as shown in Figure 9, confirming the applicability of the pseudo-second-order equation. Values of k_2 and equilibrium adsorption capacity q_e were calculated from the intercept and slope of the plots of t/q_t versus t, respectively. The values of R^2 and q_e also indicated that this equation produced better results (Table 3). R² values for pseudo-second-order kinetic model were found to be higher (between 0.994 and 0.996), and the calculated q_e values are mainly equal to the experimental data. This indicates that the adsorption system of COP obeys the pseudo-second-order kinetic model for the entire sorption period. Figures 8 and 9 show the pseudofirst-order and pseudo-second-order models of adsorption for 50 mL of 100 mg L⁻¹ of violet B and violet 5R and 0.4 g of COP at room temperature. Table 3 also shows the kinetic parameters of adsorption of violet B and violet 5R dyes onto COP. It was observed that the pseudo-second order rate constant (k_2) increased with increasing of temperature from 6.60×10^{-5} to 7.60×10^{-5} for VB and 1.965×10^{-4} to 4.86×10^{-5} 10⁻⁴ for violet 5R, respectively. Activation energies 5.47 and 29.7 KJ mol⁻¹ were determined for violet B and violet 5R, respectively. Results show that the adsorption of violet 5R is more favorable than VB onto COP.

3.8. Effect of Ionic Strength. The wastewaters released into the environment from different industries may contain various types of salts besides dyestuffs and that is why the effect of ionic strength upon the uptake of dye was studied by adding KCl, Na₂SO₄, and NaNO₃ solutions. In order to do some experiments, 50 mL of each dye and 100 mg L⁻¹ at pH 12 were used and 0.10 g adsorbent was added. The adsorption amount of azo dyes decreased with increasing of KCl and NaNO₃ concentrations in the solution from 0.1 to 1 M. This can be explained by the fact that the cations (K⁺ and Na⁺)

Table 3: Kinetics parameters for the removal of violet B and violet 5R by COP (50 mL of 100 mg L ⁻¹ of violet B and violet 5R and 0.4 g of COP	,
at room temperature).	

Sample	Fir	st order	Secor	nd order
Sample	R^2	$k_1 \ (\ { m s}^{-1})$	R^2	$k_2 (\mathrm{g mg^{-1} min^{-1}})$
VB	0.950	1.9×10^{-5}	0.994	6.6×10^{-5}
V5R	0.966	3.2×10^{-5}	0.996	1.965×10^{-4}

TABLE 4: Comparison of maximum adsorption capacities of orange peel with different dyes.

Name of pollutant	Maximum adsorption $(mg L^{-1})$	Reference	Name of pollutant	Maximum adsorption (mg L ⁻¹)	Reference
Direct blue-86	33.78	[24]	Methyl violet	11.5	[28]
Methylene blue	18.6	[28]	Amido black	7.9	[28]
Rhodamine B	14.3, 3.23	[29, 30]	Direct red 80	21.05	[31, 32]
Congo red 14.0	14.0, 22.4	[29, 30]	Direct red 23	10.72	[31, 32]
Acid violet 17	19.88	[28, 30]	Violet B	49.2	This study
Acid violet 1/	19.88		Violet 5R	87.26	This study

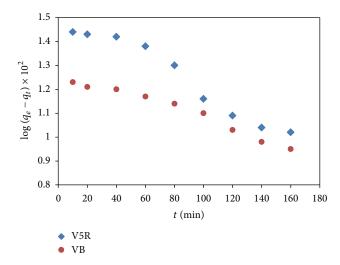


FIGURE 8: Pseudo-first-order kinetic model for violet B and violet 5R adsorption onto COP.

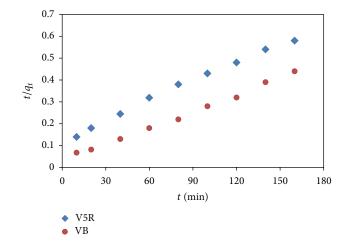


FIGURE 9: Pseudo-second-order kintic model for violet B and violet 5R adsorption onto COP.

from the salts compete with dye ions for the active adsorption sites of COP so the electrostatic interactions between dyes and surface functional groups of COP, were impeded in the presence of ionic strength. On the other hand, the Na_2SO_4 salt causes an increase in the degree of dissociation of the dye molecules by facilitating the protonation. The adsorbed amount of dyes increased as the dissociated dye ions left free for binding electrostatically onto the oppositely charged COP surface [37, 38].

3.9. Desorption. The economic possibility of adsorbent is one of the major concerns among its applications. It is widely estimated by the reusability of adsorbent. The COP is simple to thermally regenerate and regeneration temperature is commonly at or beyond 500°C. The good regeneration result and relatively low regeneration temperature demonstrated that the COP could offer high adsorptive activity. The adsorption capacity of the COP for dyes after its regeneration has also been studied. The regenerated samples of COP were again saturated with violet B and violet 5R with the same initial concentration of 100 mg L⁻¹, determining their new adsorption capacity. Generally, the adsorption capacity of the COP decreases as the number of regeneration cycle increased.

Further, our experiment also displays that the adsorption capacity could maintain above 95% of its initial capability for violet 5R and 90% for violet B after five cycles and above 80% of its initial capability for violet 5R and 75% for violet B after 8 cycles. The result here illustrates that COP can be employed repeatedly for the removal of dyes.

3.10. Comparison of COP with Other Adsorbents. The comparison of maximum adsorption capacities of some dyes with orange peel is shown in Table 4. COP in this study possesses reasonable adsorption capacity in comparison with other sorbents. COP is inexpensive agricultural waste material with rapid rate and high adsorption capacity. It is also friendly environment sorbent.

4. Conclusions

Low-cost activated carbon from orange peel was prepared as adsorbent for adsorption of azo dyes from aqueous solutions. Activated carbon developed from orange peel can be attractive options for dye removal from diluted industrial effluents. The results of this study can be summarized as follows: activated carbon developed from orange peel is a promising adsorbent for removal of the azo dye (violet B and violet 5R) from wastewater. A small amount (0.4 mg/50 mL) of COP could almost remove over 75% of 100 mg L⁻¹ of violet B and violet 5R within 30 min contact time. The pH is important in the controlling of adsorption. The Langmuir and Freundlich adsorption models were used to express the sorption phenomenon of azo dyes. The data obtained were in good agreement with the Langmuir isotherm model. The kinetic study of violet B and violet 5R on COP was investigated using pseudofirst-order and pseudo-second-order equations. The results indicate that the adsorption kinetics follow the pseudosecond-order rate and $\bar{k}_{2({\rm V5R})} > k_{2({\rm VB})}$. The used COP could be regenerated. The result illustrates that COP can be employed repeatedly after 8 cycles for the removal of dyes. It can be concluded that COP may possess a potential application in violet B and violet 5R adsorption. The present study concludes that the COP could be employed as low-cost adsorbent as alternative to commercial activated carbon for the removal of color and dyes from water and wastewater in general and for the removal of azo dyes.

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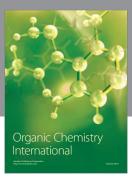
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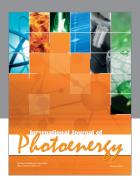
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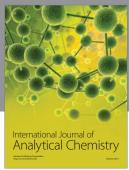
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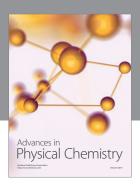
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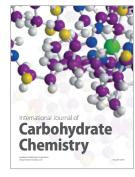
















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