Pretreated Fruit Peels as Adsorbents for Removal of Dyes from Water

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Abstract. This research focused on the development of adsorbents based on cheap, abundant and locally available agricultural wastes in Viet Nam to remove dyes from aqueous solution. In details, the effects of initial concentration (100-600 ppm), initial dose of adsorbent (0.1-1.5 g) and contacting time on the adsorption behaviors of Rhodamine B onto different kinds of pretreated fruit peel wastes, including orange peels, pomelo peels, passion-fruit peels, were evaluated. It was found that these bio-peels efficiently adsorbed in a short time, within one hour. The dye removal efficiency of orange peels and passion fruit peels ranged from 82-92% while that of pomelo peels was faster with 91-94% depending on the initial concentration (200 ppm). The efficiency of dye removal increases significantly as adsorbent dosage increases, passion-fruit peels 43-98%, pomelo peels 67-94%, orange peels 57-93%. Equilibrium adsorption results obeyed well the Freundlich isotherm; according the adsorption capacity was determined in the order: passion-fruit peels > orange peels > pomelo peels.

1. Introduction
One of the major problems faced by many countries around the world is the increase in industrial activities releases effluents containing pollutants such as heavy metal ions, organic dyes and pharmaceuticals into the aquatic environment, which cause significant health hazards to living organisms and overall deterioration of the environment [1]. Special, the treatment of dyed water is not only important but also challenging task that many countries in the world have to face. In Viet Nam, progressive activities of dye consuming and manufacturing such as textile, leader, paper, petroleum, printing, cosmetics, paint, rubber, plastic and food processing has generated increasing colored effluents containing organic dyes and other toxic compounds [2]. Because most of the organic dyes molecular pollutants are stable, small in size and not biodegradable, it is difficult to eliminate them from wastewater [3]. Many wastewater treatment methods such as chemical coagulation, photodegradation, precipitation, flocculation, activated sludge, adsorption, absorption, membrane separation and ion exchange processes have been tested for removing the pollutants [1], [4]-[6].Among various treatment methods suggested for colored effluents [2], [7], the adsorption is most favored due to its easy operation, sufficient efficiency, reasonable cost and feasibility for large-scale applications.
There are a variety of adsorbents developed for dye removals that have been studied. Activated carbons are used most widely but their applications are quite limited due to its relative high cost. In recent years, its has been found that the cheap, highly abundant agriculture wastes could be transformed to very efficient adsorbents to purify polluted water. Adsorption capacities of many different kinds of agriculture wastes, such as fruit peels, sugar cane bagasse, avocado, hami melon, dragon fruits and rice husk for a number of hazardous substances have been widely study [7]-[9]. Owing to the multifunctional characteristics of bio-peels, the adsorption of pollutants is facilitated by a combination of processes, involving ion exchange, complexion and electrostatic interactions [10], possibly low-cost and efficient adsorbents targeted for remediation of dye-polluted water. In this study, we investigated the possibility of removing organic dyes, the rhodamine B, using three kinds of tropical fruit peels including orange, pomelo, passion-fruit peels. The adsorption behaviors were described using Langmuir and Freundlich isotherm models.

2. Materials and methods

2.1. Chemicals and instruments
The synthetic dyes were purchased from HiMedia Laboratories Pvt. Ltd. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were purchased from Xilong Chemical Co, Ltd. The morphology of material was identified by scanning electron microscope (SEM) technique on the instrument S4800, Japan. The IR spectra were recorded in the range of 4000-400 cm\(^{-1}\) using a Bruker ALPHA FT-IR (Fourier transform infrared) spectrophotometer using KBr as a matrix. The concentrations of organic dyes in the solution were analyzed using an UV-VIS spectrophotometer (Shimadzu-1601 PC spectrophotometer).

2.2. Preparation of adsorbents
The bio-peel wastes, including orange peels, pomelo peels, passion-fruit peels were collected from the local market in Ho Chi Minh City, Viet Nam. The raw peels were cut into small pieces of about 2x2mm, washed with distilled water to remove adhering substances and dust followed by drying in the oven 80°C. The peel wastes were then treated by 0.01 M NaOH and 2-propanol solution [11]. After all, the pretreated bio-peels were washed thoroughly with distilled water and dried in the oven at 80°C for 24h.

2.3. Batch adsorption studies
In batch adsorption experiments, the treated peels were added into 250-mL Erlenmeyer flasks containing 100mL solution of known dye concentrations. The dye concentrations were studied from 100 to 600 ppm at a constant dried adsorbent dosage of 10g/L. All adsorption experiments were performed at ambient temperature (30 ± 2°C) using an orbital shaker operating at 180 rpm until obtaining equilibrium state in 1 hour. The mixture after adsorption was separated by centrifugation at 4000 rpm. The dye concentration (ppm) was determined via absorbance at a constant wavelength (554nm) using an UV-VIS spectrophotometer. The calibration curves were constructed by plotting the absorbance of each single dye against dye concentration at the fixed wavelength.

The percentage removal of pollutant was calculated as follows:

\[
\text{Removal efficiency} \% = \left(1 - \frac{C_e}{C_o}\right) \times 100
\]

Where \(C_o\) and \(C_e\) are the initial and residual dye concentration (ppm), respectively.

The dye uptake at equilibrium \(q_e\) (mg dye/g sorbent) was calculated as follow:

\[
q_e = \frac{C_o - C_e}{m_a} \times V
\]

Where \(C_o\) and \(C_e\) are the intial and equilibrium dye concentrations (ppm), respectively, \(V\) is the volume of solution (L), and \(m_a\) is the adsorbent dosage (g).

2.4. Adsorption isotherms
The adsorption models are powerful tools to give some insights into adsorption process and to derive important parameters revealing adsorption mechanism. Among a number of isotherm models, Langmuir and Freundlich isotherms are the most commonly used models [12]. The Langmuir model is based on the assumption that monolayer adsorption occurs on a homogeneous surface with a finite number of adsorption sites and negligible mutual interactions between the adsorbed molecules [13, 14]. The linear form of Langmuir equation is given as:

\[
\frac{1}{q_e} = \frac{1}{q_m K_L C_o} + \frac{1}{q_m}
\]  

(3)

Where: \( C_o \) (mg/L) and \( q_e \) (mg/g) are equilibrium concentration and adsorption capacity, respectively. \( q_m \) (mg/g) and \( K_L \) (L/mg) are the maximum adsorption capacity and rate of adsorption (Langmuir constants), respectively.

The essential characteristics of the Langmuir isotherm can be interpreted via the dimensionless equilibrium parameter (\( R_L \)) which is defined by:

\[
R_L = \frac{1}{1 + K_L C_o}
\]  

(4)

Where: \( K_L \) (L/mg) is the Langmuir constant and \( C_o \) (mg/L) is the highest initial concentration. The type of the adsorption isotherm is determined by the value range of \( R_L \): unfavorable (\( R_L > 1 \)), linear (\( R_L = 1 \)), favorable (\( 0 < R_L < 1 \)) and irreversible (\( R_L = 0 \)) [9, 15].

The Freundlich model assumes that molecules are adsorbed on the heterogeneous surfaces of adsorbent based on different sites with different adsorption energies [16]. This model takes into account the mutual interaction between adsorbed molecules. The application of the Freundlich equation also suggests that sorption energy exponentially decreases upon the completion of the sorption centers of the adsorbent. The linear form of Freundlich equation is given as:

\[
\ln q_e = \ln K_F + \frac{1}{n} \ln C_o
\]  

(5)

Where: \( 1/n \) and \( K_F \) [(mg/g).(L/mg) \( 1/n \)] are Freundlich constants related to the favorability of adsorption process and the adsorption capacity of the adsorbent, respectively. The heterogeneity factor, \( 1/n \) expresses adsorption intensity of adsorbent; the adsorption bond is stronger with decreasing \( 1/n \) value.

3. Results and discussion

3.1. Characterization of biosorbents

The functional groups on the peels were studied using FT-IR spectrophotometry in the range of 4000 to 400 cm\(^{-1}\) (Figure 1). The broad band observed at 3076-3580 cm\(^{-1}\) for all three peels matches the O-H stretching frequency, it can originate from intermolecular hydrogen bonds linking the compounds and alcohols, phenols and carboxylic acids. The strong adsorption of about 763-1776 cm\(^{-1}\) in accordance with the frequency of functional groups lasted aromatic C-H and C=O groups linked compounds aldehydes, ketones, esters, amides, carboxylic acids. The peak at 1055 cm\(^{-1}\) clearly shows the presence of the C-O group in the carboxylic and alcoholic. Peaks observed at around 2920 cm\(^{-1}\) can be attributed to the C-H stretching frequency. The relatively wide central peak of about 1664 cm\(^{-1}\) stems from the extension of the C-C aromatic ring. The adsorption peaks in the range of 1000-1300 cm\(^{-1}\) can be considered for angular deformation in the bonding plane of C-H aromatic rings. In addition, consecutive peaks in the 3672-4000 cm\(^{-1}\) range may be assigned to the N-H bond. It can be seen that the surface of biosorbents contains functional groups.
such as hydroxyl and carboxyl groups necessary for the adsorption of dye molecules [17], [18]. In the SEM micrographs, all bio-peels possessed the typical structure of plant based cellulosic materials with highly rough, and irregular structure according to SEM analysis (Figure 2).

3.2. Effect of initial adsorbent dosage
Rhodamine B dye solutions (100 mL) of concentrations (200ppm) were mixed with passion-fruit, pomelo, orange peels of different dosage (0.1-1g) in separate vials. Experimental factors such as the adsorbate concentration used, agitation speed and temperature were kept the same. Figure 3 show for all three kinds of peels, the percentage removal reached the highest level at 1.5g, decreased slightly at 1g and 0.5g but rapidly dropped upon further decrease in dosage to 0.1g. The passion-fruit peels appeared as the best adsorbent among three kinds of bio-peels; the removal efficiencies were determined to be 42.4%, 94.3%, 96.8% and 97.9% at 0.1g, 0.5g, 1g and 1.5g respectively. The pomelo peels and orange peels were as efficient as passion-fruit peels in removal effect of rhodamine B dye over 90% with initial adsorbent dosage over 0.5g.

3.3. Effect of initial adsorbate concentration
In this study, rhodamine B dye solutions (100 mL) of different concentrations (100-400ppm) were mixed with three kinds bio-peels (1g) in separate vials. Effect of initial rhodamine B concentration on removal efficiency using treated fruit peels is presented in Figure 4. For all three kinds bio-peels in removal effect over 90% with initial adsorbate concentration 100-400 ppm, highest at 100 ppm (pomelo peels 98.7%, passion-fruit peels 98.3%, orange peels 92.4%) and decrease slightly at 200-400 ppm. The efficiency of the fruit peels decreased sharply when the concentration increased to 600 ppm (pomelo peels 57.4%, passion-fruit peels 56.2%, orange peels 55.9%)

3.4. Effect of contact time
This experiment was conducted with different contact time (30-300 minutes), rhodamine B dye solutions (100 mL) of concentrations (200 ppm) were mixed with passion-fruit, pomelo, orange peels of different dosage (1 g) in separate vials. Figure 5 show effect of contact time on removal efficiency using treated fruit peels. The highest efficiency of passion-fruit peels is 96.8% at 300 minutes, pomelo peels is 94.2% at 300 minutes and orange peels is 93.6% at 180 minutes. Effective treatment of passion-fruit peels increases over contact time, but effective treatment of pomelo and orange peels is unstable over contact time. When the contact time over 60 minutes the removal efficiency of three kinds fruit peels is over 90%.

3.5. Effect of pH on the adsorption of different dyes.

The extraction data for pollutants using different peels at various solution pH values are shown in Figure 6. The percentage removal of pollutants changed when changing pH value, owing to the efficient exchange of cations with functional groups on the surface treated peels. All three bio-peels were effective toward removing dyes from water, reaching removal rates of 80–99%.

3.6. Isotherm studies

The experimental data were fitted with Langmuir and Freundlich isotherm models; the model constants were determined as provided in Table 1. It was found that Freundlich model best describes the adsorption behavior of rhodamine B on the bio-peels with high $R^2$ values ($0.9131-0.9967$) while the fitting to Langmuir model exhibited lower compatibility. The plot of $1/C_e$ against $1/q_e$ in Langmuir model is shown in Figure 6a with the highest correlation coefficient ($R^2=0.9967$) obtained for the orange peels. According to the Langmuir isotherms, the maximum adsorption capacities were found in the order: orange peels (312.5 mg/g) > passion-fruit peels (51.81 mg/g) > pomelo peels (38.31 mg/g). Moreover, for all three kinds of bio-peels, the $R_L$ values were lower than 1 revealing favorable adsorption processes.
Figure 7. (a) Langmuir isotherm plots; (b) Freundlich isotherm plots

Table 1. Langmuir and Freundlich model constants

| Types of peels     | Langmuir isotherm | Freundlich isotherm |
|--------------------|-------------------|---------------------|
|                    | $q_{\text{max}}$ (mg/g) | $K_L$ (L/mg) | $\text{R}^2$ | $R_L$ | $K_F$ | $n$ | $\text{R}^2$ |
| Pomelo             | 38.31             | 0.2587            | 0.8895      | 0.0064 | 7.7037 | 1.9573 | 0.9131 |
| Passion-fruit      | 51.81             | 0.1359            | 0.9834      | 0.0121 | 7.7029 | 1.9091 | 0.998  |
| Orange             | 312.5             | 0.0040            | 0.9967      | 0.2947 | 1.2896 | 1.0413 | 0.9979 |

3.7. Characterization of pretreated fruit peels after the removal dyes

To identify the mechanism of adsorption of dyes ions on the adsorbent, FTIR spectra were recorded before and after rhodamine B dyes adsorption as presented in Figure 8. The spectrum of three kinds bio-peels reveals the presence of characteristic peaks as follows: 3076-3580 cm$^{-1}$ (stretching vibration of OH), 2920 cm$^{-1}$ (stretching vibration of C-H in CH, CH$_2$ and CH$_3$), 1664 cm$^{-1}$ (stretching vibration of C=O), 1385 cm$^{-1}$ (blending and scissor vibration of CH$_3$ and CH$_2$), 1048 cm$^{-1}$ (stretching vibration of C-O), 790 cm$^{-1}$ (deformation vibration of the CH$_2$ bond). During adsorption process, there were some interactions between the bio-peels and dyes ions in the aqueous phase, consequently resulting in shifts of the characteristic peaks. As observed in Figure 8c, the peak at 3309 cm$^{-1}$ before adsorption shifted towards 3460 cm$^{-1}$ after adsorption possibly due to the bonding of OH with dyes ions. Moreover, in Figure 8b the shifts of 848, 1647, 2931, 3479 cm$^{-1}$ to 1035, 1652, 2920, 3344 cm$^{-1}$, respectively, can be easily recognized. These shifts might be ascribed to electrostatic interaction between the $\pi$ electrons of bio-peels layers and dyes ions.
4. Conclusions

Three kinds of tropical fruit peel wastes, pomelo, orange and passion-fruit peels, were investigated as potential biosorbents for the extraction of dyes in water. All three natural materials were effective toward removing dyes from water, reaching removal rates of 80−99%. Orange peels showed the highest extraction efficiency, close to 99%, toward safranine at pH=3 values. The adsorption capacity of the dyes increased with increasing contact time and a plateau was reached at equilibrium at 180 minute, implying that the adsorption process was rapid in the beginning, gradually decreased as time progressed and finally attained saturation when equilibrium was reached. The Freundlich isotherm model fitted best the adsorption process, the Langmuir isotherm model shown the maximum adsorption capacities were found in the order: orange peels (312.5 mg/g) > passion-fruit peels (51.81 mg/g) > pomelo peels (38.31 mg/g). The data indicate a monolayer adsorption occurrence at binding sites on the surface of the peels. All three peels could be used as nontoxic, renewable, low cost, efficient and effective adsorbents for water purification.

5. References

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