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Chemically Treated Orange Peels as a Bio-adsorbent for Various Dyes

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In this study, the decolorization capability of various synthetic dyes using the chemically treated orange peel (CTOP) is highly effective. An uncomplicated consecutive chemical treatment process by sodium hydroxide and iso-propanol promotes enhanced adsorption capacity of the raw orange peel for cationic dyes and enables high removal efficiencies in a wide range of pH conditions. The highest removal efficiency of the CTOP for the dyes in the pH range of 3-9 follows the order, safranin (99 %, pH 3) > methylene blue (97 %, pH 5) > methyl violet (91 %, pH 9) > rhodamine B (37 %, pH 3) > Congo red (20 %, pH 5). The adsorption capacity of CTOP for methylene blue calculated from the Langmuir model (R^2 > 0.99) is remarkably high at 294 mg/g, which is almost 1.5 times higher than that of the untreated orange peels. These results demonstrate the great potential of low-cost, effective CTOP for application in the purification of dye-contaminated water. The selective removal of certain groups of toxicants from contaminated water using bio-peels can be achieved via tailoring their surface properties as removing essential oils on surface peels to increase the pore, appearing dendrimer-like microspores.

1. Introduction

Remediation of dye-contaminated wastewater as 2-pic (Saeedeh et al., 2014), crystal violet (Xie et al., 2020) is one of the most challenging problems faced by many countries around the world (Ying, 2018). Progressive increase in dye consuming and producing industries such as textile, pharmaceutical, leader, paper, petroleum, printing, cosmetics, paint, rubber, plastic, and food (Rahmat et al., 2019) has led to the continued discharge of a huge amount of toxic wastewater containing highly synthetic dyes into to aquatic environments (Roy et al., 2012). Because of their highly stable and complex aromatic structures, dye molecules are difficult to be degraded by conventional oxidation or bio-degradation methods. These compounds in aquatic bodies result in many harmful effects such as the considerable increase in chemical oxygen demand, limitation of light penetration into the water, undesirable interference in photosynthesis of aquatic plants, prevention of microbes, microbes' growth, and micro-toxicity aquatic life. The removal of dyes from wastewater is urged (Mohammed et al., 2021). Many dyes are detrimental to humans due to their carcinogenic and mutagenic nature (Etim et al., 2016).

So far, several treatment methods for coloured effluents had been applied, including adsorbent (Yixi et al., 2018), photocatalytic degradation, biodegradation (Adeyi et al., 2019), ozonation, membrane-filtration, ion-exchange, chemical precipitation (Anastopoulos and Kyzas, 2014). The large-scale applications of such methods are still not feasible because of either high cost or low efficiency (Roy et al., 2012). In recent years, the agriculture waste-based adsorbents as cellulose aerogel (Yixi et al., 2018), activated carbon (Saeedeh et al., 2014), pre-treated fruit peel waste (Nguyen et al., 2019) to purify dye-polluted water had gained much attention. These are cheap, highly abundant, efficient, and viable for regeneration. Based on multifunctional characteristics of bio-peels, adsorption of toxicants is afforded via interactive steps, possibly involving ion

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exchange, complexation, and electrostatic interactions (Ramakrishna et al., 2015). Hence, a large number of studies have been performed to explore the intrinsic adsorption capacities of many different kinds of agriculture wastes, such as pineapple (Luu et al., 2020), sugarcane bagasse (Quoc et al., 2020), pineapple leaf and cotton waste (Nga et al., 2021), coconut coir dust (Etim et al., 2016), and cotton (Yixi et al., 2018). The chemically pre-treated avocado, Hami melon, and dragon fruit peels were reported to offer high efficiency in removing dyes and toxic heavy metals (Yingchun et al., 2016). The cheap, abundant orange peel waste has attracted much attention as an efficient bio-sorbents for many toxicants (Roy et al., 2012).
In this paper, the adsorption capacities of the chemically pre-treated orange peels are investigated for several common dyes including Congo red (CR), methylene blue (MB), methyl violet (MV), safranin (S), rhodamine B (RB). The parameters involved, such as equilibrium time, pH, adsorbent dose, initial dye concentration is evaluated.

2. Materials and method

2.1 Materials

The synthetic dyes including CR ($C_{32}H_{22}Na_2N_6O_6S_2$, 99.5 %), MB ($C_{16}H_{18}ClN_3S.3H_2O$, > 99 %), MV ($C_{25}H_{30}ClN_3$, 99.5 %), S ($C_{20}H_{19}N_4Cl$, 99.5 %) were purchased from Hi Media Laboratories Pvt. Ltd. Sodium hydroxide (NaOH, 90 %), hydrochloride acid (HCl, 36.5 %) and iso propanol (C_3H_8O, 99.7 %) were procured from Xilong Chemical Co, Ltd. RB ($C_{28}H_{31}ClN_2O_3$, >95 %) was supplied by Sigma-Aldrich Co.

2.2 Preparation of CTOP

Fresh orange peels were collected from juice shops in Ho Chi Minh City, Vietnam, then cut into small pieces of 2×2 mm. The chopped orange peels were washed with distilled water to remove adhering substances before drying in the oven at 80 °C (ROP). The chemical treatment of the orange peels was conducted via two steps, including immersion 0.02 M NaOH solution to establish more hydroxyl groups onto the peel surface and extraction of soluble organics using iso-propanol. ROP was washed thoroughly with deionized water until pH 7 (in not to affect the pH results in the next adsorption experiments) and dried in the oven at 80 °C for 24 h (CTOP).

2.3 Structure and morphologies analysis

The Fourier transform infrared spectra (FT-IR) was recorded in the range of 4,000 - 400 cm^{-1} (Alpha-E, Bruker, Germany) using KBr as a matrix. The surface morphology of ROP and CTOP before/after adsorption of MB were established using field emission Scanning Electron Microscopy (SEM) (The Thermo Scientific Prisma E SEM). Before measurement, the samples were coated with a thin platinum layer for 30 s by using a sputtering machine.

2.4 Adsorption studies

100 mL dye solution of known concentrations was contacted with CTOP in 250 mL Erlenmeyer flasks. The examined dye concentration (100 - 600 mg/L) is similar to reality dye content in a studying factory with bio-sorbent mass in the range of 0.1 - 1.5 g. The pH of the stock solution was varied by adding either 0.1 M HCl or 0.1 M NaOH. All adsorption experiments were performed at ambient temperature (30 ± 2 °C) using an orbital shaker operating at 180 rpm until attaining an equilibrium state. The mixture after adsorption was separated by centrifugation at 4,000 rpm. The dye concentration (mg/L) was determined via absorbance at a particular wavelength for each dye (664 nm for MB, 518 nm for S, 554 nm for RB, 583 nm for MV, 500 nm for CR using a UV-Vis spectrophotometer (Shimadzu-1,800). CTOP and solution before/after adsorption of MB are shown in Figures 1a and 1b. The calibration curves are constructed by plotting the absorbance of every single dye against the dye concentration at the fixed wavelength.

(a)  (b) 

Figure 1: (a) CTOP and (b) MB 100 mg/L before and after adsorption

The percentage removal of the pollutant is calculated by the following Eq(1) (Etim et al., 2016).

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

where C_0 and C_t are the initial and residual dye concentrations (mg/L).
The dye uptake at equilibrium q_e (mg dye/g sorbent) is calculated by the following Eq(2) (Etim et al., 2016).

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

where C_0 and C_e are the initial and equilibrium dye concentrations (mg/L), V is the volume of solution (L), and m is the adsorbent dosage (g).
The Langmuir and Freundlich isotherm models are used to investigate the adsorption mechanism and maximum adsorption capacity. The following Eq(3) and Eq(4) present the linear equations of the isotherm models (Yixi et al., 2018).

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{K_L q_{max}} \quad (3)$$

$$lnq_e = lnK_F + \frac{lnC_e}{n} \quad (4)$$

where equilibrium constants K_L, K_F are fitted for Langmuir and Freundlich models; q_{max} represents the maximum capacity of adsorbent for dye (mg/L).

3. Results and discussion

3.1 The capability of CTOP to remove various common dyes

To investigate the capacity of CTOP for removing various dye compounds, including RB, MV, CR, and S which have been extensively used in pharmaceuticals. Since the adsorption capacity of the absorbent can largely vary depending on the pH of the solution. The batch adsorption studies are performed at different pH values, with the constant CTOP dosage of 10 g/L and a dye concentration of 200 mg/L. According to the results shown in Figure 2, the CTOP adsorbs strongly the cationic dyes including MB, MV, and S. In the pH range of 3 - 9, the pH of the solution does not significantly alter the adsorption of MB and S. The removal of MV has a slightly rising trend with enhancing pH, but RB showed a reverse direction as may be affected by -COOH functional group of RB structure. The adsorption of an azo dye, CR appeared significant only in the near-neutral pH region. The favour of adsorption on CTOP generally follows the order, S > MB > MV > RB > CR. The highest removal efficiencies are, approximately, 99 % for S at pH 3; 97 % for MB at pH 5; 91 % for MV at pH 9; 37 % for RB at pH 3 and 20 % for CR at pH 5. The modified surface by chemicals leads to the difference in the order of adsorption efficiency between CTOP and the raw orange peel in a previous study, which is reported to adsorption CR, and RB much better than MV (Gurusamy et al., 2002).

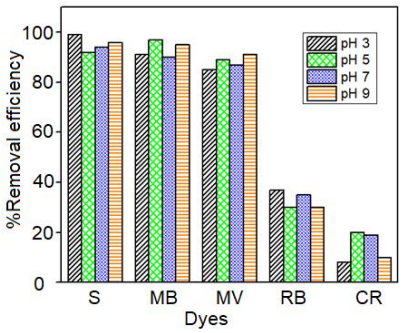

Figure 2: Removal efficiencies of various dyes by CTOP

The dominant adsorption of cationic dyes including S, MB, and MV, and high removal efficiencies obtained in an acidic environment is likely due to the increased amount of phenoxide and carboxylate groups resulted from the pre-treatment. Because of two (-NH_2) groups in the molecular structure, S has the greatest electron affinity and strongest linking with CTOP. In terms of spatial structures, the MB molecule which is not as bulky as the MV and RB molecule easily fills the pore on CTOP. CR is a benzidine-based anionic diazo dye that the removal efficiency is the lowest. The adsorption mechanism is primarily based on a strong electrostatic force between the amount of negatively charged groups of surface material and the positively active sites of the

dye, particularly cation dyes. Essential oils of orange peels are eliminated by iso-propanol in the pretreatment process, which causes appearing lot of pores to contain dye molecules. Compared to other adsorbents with performance depending much on the pH of the solution, the low-cost CTOP can offer high adsorption capacities towards cationic dyes and relatively stable adsorption capacities on a wide pH scale. It can be considered a very promising adsorbent for removing dyes from practical environments that generally have a certain degree of pH fluctuation.

3.2 Structure and morphologies of bio-adsorbent

To investigate the structure of the bio-absorbent, the FT-IR analysis is conducted on ROP and CTOP. As shown in Figure 3, the broadband observed in the range of 3,530 - 3,120 cm^{-1} corresponds to the O-H stretching frequency, which may originate from inter and inter-molecular hydrogen bonding of polymeric compounds, alcohols, phenols, and carboxylic acids. The peaks at 2,917 and 2,850 cm^{-1} can be ascribed to the C–H stretching and in the range of 1,645 - 1,620 cm^{-1} prove the presence of carbonyl groups stretching from carboxylic acids and ketones, which are conjugated and non-conjugated to aromatic rings. The adsorbent bands in the range of 1,100 - 1,000 cm^{-1} correspond to the axial C-O bond (Ramakrishna et al., 2015). The surface of bio-sorbents contains functional groups such as hydroxyl and carboxyl groups necessary for the adsorption of dye molecules.
In addition, Figure 3 compares the chemical bonds on the surface of CTOP before and after MB adsorption. The chemical treatment and MB adsorption induced change mainly in the 3,530 - 3,100 cm^{-1} characteristic of O-H stretching and 1,100 - 1,000 cm^{-1} characteristic of C-O bonding, indicating an important role of such groups in the adsorption process. The peak in the region of 1,200 - 1,000 cm^{-1} of CTOP deconvoluted to more clear individual peaks with the soonest one occurring at 1,025 cm^{-1}; the band for O-H stretching is also changed, from 3,518 - 3,120 to 3,530 - 3,258 cm^{-1}. These differences can indicate the fill of dye on CTOP. After adsorption, the peaks at 1,009 and 3,120 cm^{-1} become unclear again, presumably due to the interaction with MB molecules.

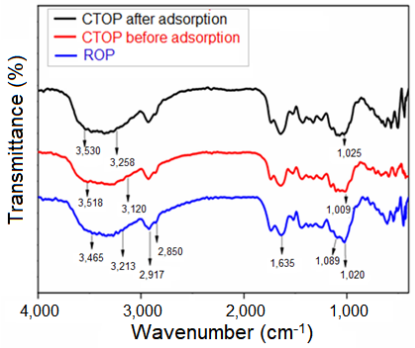

Figure 3: FT-IR spectra of the raw orange peel, CTOP before and after adsorption of MB

The SEM images (Figure 4a and 4b) reveal the morphological features and surface of plant-based cellulosic materials. Many dendrimer-like macrospores with high roughness and irregularity are revealed to exist on the surface of orange peels after treatment by NaOH and iso-propanol. Notable differences in the morphology of ROP and CTOP are observed to enhance the wrinkles, and surface area leads to highly efficient surface adsorption. After adsorption, MB applies the pore on the material's surface, so the dendrimer-like macrospores disappeared (Figure 4c).

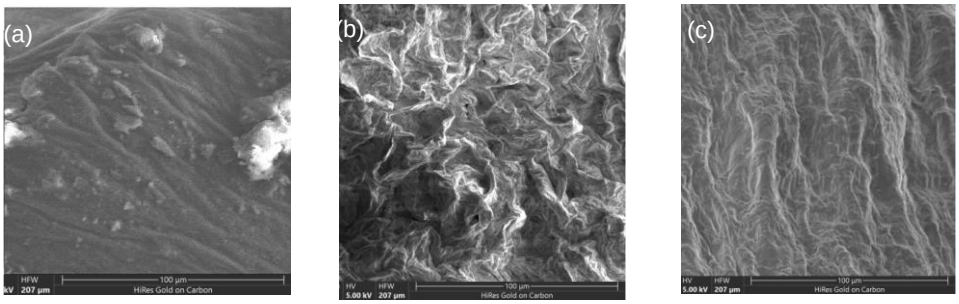

Figure 4: SEM images of (a) the ROP, (b) CTOP before, and (c) after adsorption of MB

3.3 Effect of bio-adsorbent for MB

The effect of the pre-treatment condition is first evaluated via batch experiments for adsorption of MB on the orange peels. It is found that the equilibrium is established after 3 h and then the removal remained unchanged; thus, the contacting time of 3 h is selected for further experiments (Nguyen et al., 2019). In an attempt to enhance the adsorption capacity of ROP, chemical treatment of the raw bio-peel surface using NaOH and iso-propanol is applied.

Figure 5 depicts the comparison of ROP and CTOP on adsorption efficiency (Figure 5a) and the influence of adsorbent CTOP dosage at different initial dye concentrations (Figure 5b).

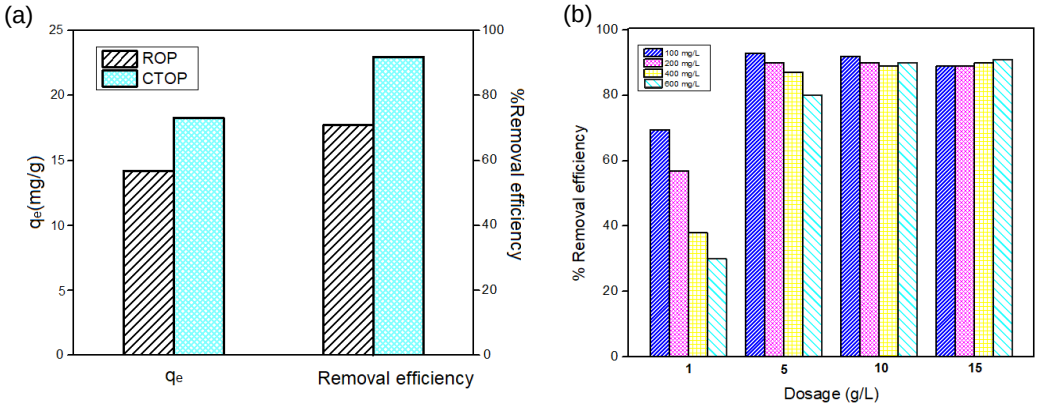

Figure 5: (a) Effect of pre-treatment on adsorption efficiency of the orange peel, (b) Effect of adsorbent dosage at different initial dye concentrations

The higher amount of surface-bound hydroxyl groups resulted from NaOH treatment and the large number of adsorption sites left behind due to the extraction of soluble organics using iso-propanol cause effectively toward removing dyes. As shown in Figure 5a, the removal efficiency for MB goes up from 71 % to 92 % with a 4.3 mg/g increase in dye uptake when adsorption experiments are compared ROP with CTOP. Figure 5b shows the effect of initial MB concentration (100 - 600 mg/L) and CTOP dosage on removal efficiency and adsorption capacity. At the concentration of 100 mg/L, the removal percentage obtains at 69.5 % (CTOP dosage of 1 g/L), but it increases significantly to about 93 % (CTOP dosage of 5 g/L). And then, the removal efficiency remains almost stable despite the further addition of CTOP. There is a notable decrease in removal efficiency if increasing the initial MB concentration and keeping CTOP dosage of 1 g/L. With higher dye concentration, the increase in CTOP dosage obviously leads to higher efficiency, and the saturation level is determined at the CTOP dosage of 10 g/L. The highest removal efficiency fluctuates around 90% in the concentration range of 100 - 600 mg/L.

The adsorption parameters analyzed from the Freundlich and Langmuir isotherm models are shown in Table 1

Table1: Isotherm parameters for MB adsorption on CTOP

	Langmuir isotherm			Freundlich isotherm		
q_{max}	K_L	R^2	R_L	K_F	n	R^2
294	0.0041	0.9934	0.2773	4.6912	1.6204	0.9821

As presented in Table 1, the Langmuir model can be used best to describe the adsorption behaviour of MB on the CTOP, as evidenced by a high correlation coefficient with R^2 of 0.9934. The maximum adsorption capacity is defined to be 294 mg/g, which is significantly higher than the value of the natural orange peels reported in the previous studies (Boumedience et al., 2015). The R_L of approximately 0.2773 < 1.0000 indicates favorable adsorption of MB on CTOP. The fitting to the Freundlich model has a lower correlation coefficient, R^2 of 0.9821. The n value of 1.62 also demonstrates the beneficial adsorption process (Yixi et al., 2018).

4. Conclusions

It has been found that CTOP enriches in surface functional groups has a great potential for application in the treatment of dye contaminated effluents as it is capable of adsorbing effectively cationic dyes over a wide range of pH (3 - 9). The removal efficiencies generally follow the order S, MB, MV, RB, CR. The adsorption capacity of MB was found to increase by about 1.5 times after pre-treatment, with the initial dye concentration

of 200 mg/L, adsorbent dosage of 10 g/L. These results demonstrate the potential of low-cost, effective CTOP for water purification and demonstrate the potential of low-cost, effective CTOP for water purification and suggest the possibility of tailoring bio-peel surface towards either enhanced adsorption or desired selectivity for removal of certain groups of toxicants from contaminated water.

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