

Removal of Reactive Yellow 145 from simulated dye wastewater by *Theobroma cacao* pod-derived adsorbents

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Abstract Industrial processes that discharge great quantities of reactive dyes in recipient waters merit the advancement in the color removal in wastewaters. This study produced activated carbon from *Theobroma cacao* pods, a waste from cocoa processing and used to remove Reactive Yellow 145 (RY 145) from simulated textile wastewater in batch experiments. The effects of operating parameters such as adsorbent dose, initial dye concentration and contact time on the adsorption of residual RY 145 were evaluated. CCD was used to optimize these operating parameters resulting to 90% removal of RY 145 after 1.5 h. Chemisorption was the dominant adsorption mechanism in this study as indicated by the high correlation of experimental data with both the Temkin isotherm ($R^2=0.978$) and the pseudo second-order kinetic model ($R^2=0.999$). Results suggest that CPAC can be an alternative for the treatment of dye-contaminated wastewaters.

Keywords: Adsorption; activated carbon; cocoa pods; reactive yellow 145; dye wastewater; optimization

1. Introduction

Localized dyeing is the printing design on fabrics that involves large amount of finishing agents used for softening, crosslinking and waterproofing. These finishing methods contributes in water contamination (Kurniawan and Lo 2009). It contributes to a serious water environmental concern. The dye discharge in the effluent is approximately 10-15% dye (Dizge *et al.* 2008). Synthetic dyes are tough to destroy due to their synthetic origin and aromatic structures (Wang *et al.* 2011). Dyes hinder the passage of sunlight in receiving waters, limit reoxygenation from the photosynthetic activity (Xie *et al.* 2011) and interrupt biological activities in water bodies (Messina and Schulz 2006). It may be mutagenic, allergenic, carcinogenic and toxic to aquatic organisms depending on their chemical structure (Akar *et al.* 2009). Various methods such as adsorption (Mahmoodi *et al.* 2010), nanofiltration (Amini *et al.* 2011), precipitation, ion-exchange, electroflotation, membrane filtration, electrocoagulation, and electrochemical oxidation, were used to treat colored wastewaters (Mittal *et al.* 2007). But these methods need high operating costs and capital

investments that are incapable of treating an extensive variety of dye wastewaters (Lata *et al.* 2007).

In recent years, activated carbon can be regarded as good adsorbent for different adsorbates due to its high microporosity with high surface area. Due to its low capital cost, simple experimental design and ease of operation which renders the process more superior to other techniques in some respects (Tehrani-Bagha *et al.* 2010). Therefore, low-cost substitutes such as wood wastes, clay materials, fly ash, and agricultural by-products have been the subject of various adsorption studies (Theivarasu and Mysamy 2010). Agricultural remains such as peanut hull (Tanyildizi 2011), thespesia populnea pods (Arulkumar *et al.* 2011) palm ash (Isa *et al.* 2007), citrus fruit peel (Dutta *et al.* 2011) rubber wood sawdust (Kalavathy *et al.* 2009) coconut shells, almond shells, peach stones, grape seeds, apricot stones, cherry stones, olive stones, nut shells, rice husks, resackwood, and oil palm shells (Khorramfar *et al.* 2011) had been tested for their capabilities of removing dyes. There are 36 million tons of cocoa pod wastes generated from bean production of *Theobroma cacao* worldwide in 2010 (WCF 2014). From the waste pods of cocoa processing, a low-cost dye adsorbents can be made.

This study focusses on the use of cocoa pods activated carbon (CPAC) to remove the Reactive Yellow 145 (RY 145) from aqueous solutions. The effect of initial RY 145 concentration, adsorbent dosage, and contact time were investigated. To study the controlling mechanism of the sorption process, pseudo first-order, pseudo second-order kinetic model was used. Central composite design (CCD) was used to optimize batch adsorption operating parameters. Langmuir, Freundlich, Temkin, and Dubinin-Raduskevich adsorption isotherms were used for experimental sorption data evaluation.

2. Materials and methods

2.1 Preparation of CPAC

Sundried cocoa pods were obtained from Menzi Agricultural Corporation, Bukidnon, Philippines. The pods were washed with deionized water, oven dried at 50°C for 1 hour, and pulverized using a Wiley mill. The resulting powder was screened using a test-sieve shaker to obtain particles from 300-500 µm in diameter. The powder was soaked in 0.317 M HNO₃ for 24 h and rinsed at room temperature for adequate surface oxidation (Zhang and Itoh 2003). The mixture was oven dried at 105°C for 2 h and then carbonized at 400°C for 3 h. The carbon residues were washed with deionized water until pH 7 was achieved and the slurry was dried at 105°C to a constant weight.

2.2. Preparation of RY 145 dye solution

All reagents were prepared using deionized water. Reactive Yellow 145 dye (C₂₈H₂₀ClN₉O₁₆S₅·4Na, Trust) was used without further purification. The RY 145 stock solution was prepared at different concentrations based on the experimental designs. The residual concentrations of RY 145 was determined using a UV-vis spectrophotometer (Shimadzu Mini 1240) at λ_{max}=416 nm based on the established absorbance and concentration relationship.

2.3. Batch adsorption experiments

In an Erlenmeyer flasks, 50-mL of RY 145 solution of known concentrations and corresponding CPAC dosages were agitated using a gyratory shaker at 200 rpm at different periods according to the experimental design. Batch experiments were done at room temperature at varying initial RY 145 concentrations (10-30 mg·L⁻¹), CPAC dosage (0.25-1.25 g), and contact time (0.5-2.5 h). These parameters was used to determine the best combination for the optimum RY 145 removal (%) efficiency as shown in Eq. (1).

$$RY145removal(\%) = \frac{(C_0 - C_e)}{C_0} \cdot 100 \quad (1)$$

where C_0 and C_e are the initial and final concentrations of RY 145 respectively.

The kinetic study was achieved using the optimum levels of initial RY 145 concentrations (17.5 mg·L⁻¹), CPAC dose (1.0 g), and contact time (1.0 h). Samples were collected at 0, 10, 20, 30, 40, 50 and 60 minutes for filtration and residual dye concentration analysis. The final RY 145 concentration was analyzed using UV-vis spectrophotometer. The adsorption capacity, Q was calculated using Eq. (2).

$$Q = \frac{(C_0 - C)}{m_{adsorbent}} (V_{sample}) \quad (2)$$

where Q is the adsorption capacity which is the amount of solute adsorbed from the dye solution, C_0 and C are the concentrations before and after the adsorption, V is the volume (mL) of the sample adsorbate, and m is the weight (g) of the adsorbent. The data were fitted to Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich isotherm models. Sorption data were fitted to pseudo-first order and pseudo-second order.

3. Results and discussion

3.1 Effect of initial concentration on the % dye removal

An increase in initial RY 145 concentration from 15-25 mg·L⁻¹ at constant (0.5 g) CPAC dosage caused an increase in % dye removal (Fig. 1). This can be attributed to the available unsaturated adsorption sites in the CPAC particles as the initial concentration is increased (Mi-Na *et al.* 2006). The 2.0 h adsorption time at constant CPAC dosage resulted in a 20% increase in dye removal as compared with 1.0 h of treatment (Fig. 1a). Increasing the initial RY 145 concentration up to 55 mg·L⁻¹ tend to decrease the dye removal due to the increase in dye molecules that saturates the binding sites found on the surface of CPAC. The saturation of the CPAC particles was hastened by the addition of excess dye molecules that limits the adsorption sites of CPAC (Verma and Mishra, 2010).

3.2 Effect of adsorbent dose on RY 145 removal (%)

At constant contact time of 0.75 h, increasing CPAC dosage from 0.5-1.0 g resulted a 30% increase in % dye removal and with almost 20% difference between 15 mg·L⁻¹ and 25 mg·L⁻¹ initial RY 145 concentrations (Fig. 1b). At low dosage of CPAC, there is a strong competition between the RY 145 dye molecules due to inadequate amount of vacant binding sites. More adsorption sites became available as higher amounts of CPAC were introduced (Kumar *et al.*, 2010). Further increase in CPAC dosage did very little to improve the dye removal efficiencies. Similar results were observed by Feng *et al.* (2011).

3.3 Effect of contact time on the % dye removal

At 15 mg·L⁻¹ initial RY 145 concentration, the % dye removal increases as the time of adsorption process also increases (Fig. 1c). There is a progressive proliferation in adsorption of the RY 145 on CPAC surfaces. At constant CPAC dosage (1.0 g), increasing the adsorption time did not significantly improve the % dye removal. Moreover, a higher initial dye concentration generally resulted in greater dye removals but only up to a certain extent. It can be perceived that the role of the chemical activation of CPAC has provided more active sites that contributes to the higher adsorption of RY 145 dye molecules from the aqueous solution.

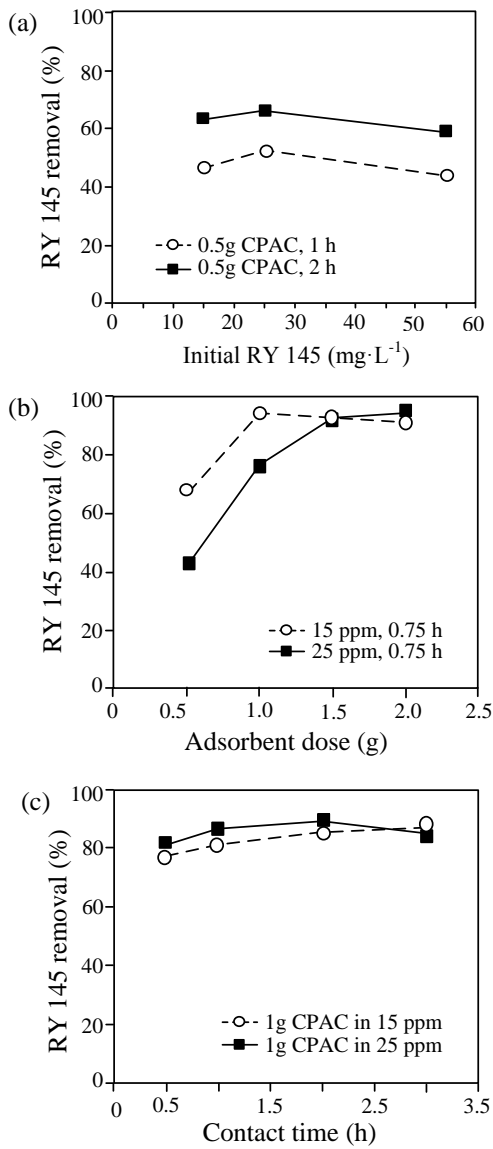


Fig. 1. Effect of (a) initial dye concentration, (b) adsorbent dose and (c) contact time on percentage removal of RY 145 dye.

3.4 Adsorption isotherm studies

The Langmuir adsorption isotherms signifies the equilibrium distribution of dye ions between solid and liquid phases (Hall *et al.*, 1966). The Langmuir isotherm is effective for monolayer adsorption onto an exterior having a limited amount of identical sites. This model Eq. (3) adopts, even drives the adsorption on the external surface and no shifting of adsorbate on the surface (Hutson and Yang 2000).

$$q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e} \quad (3)$$

q_e is the amount of dye adsorbed per gram of adsorbent at equilibrium ($\text{mg}\cdot\text{g}^{-1}$), Q_0 is the maximum monolayer coverage capacity ($\text{mg}\cdot\text{g}^{-1}$), K_L is the Langmuir isotherm constant ($\text{L}\cdot\text{mg}^{-1}$), and C_e is the concentration of adsorbate at equilibrium ($\text{mg}\cdot\text{L}^{-1}$). The Freundlich adsorption isotherm is applied to the adsorption physiognomies for the heterogeneous surface (Voudrias *et al.* 2002). The data fit frequently to the Freundlich isotherm as shown in Eq. (4):

$$Q_e = K_f C_e^{\frac{1}{n}} \quad (4)$$

where K_f is the Freundlich isotherm constant ($\text{mg}\cdot\text{g}^{-1}$), n is the adsorption intensity, C_e is the concentration of adsorbate at equilibrium ($\text{mg}\cdot\text{L}^{-1}$), Q_e is the amount of metal adsorbed per gram of the adsorbent at equilibrium ($\text{mg}\cdot\text{g}^{-1}$). The constant K_f is an estimated indicator of adsorption capacity, whereas $1/n$ is the adsorption strength function of the adsorption process (Tempkin and Pyzhev 1940).

The Temkin adsorption isotherm has consideration of the low and high concentration amounts, the model adopts that the heat of adsorption (function of temperature) of all the particles in the layer will linearly decrease instead of the logarithmic with coverage (Gunay 2007). The model is expressed in Eq. (5).

$$q_e = \frac{RT}{b_T} \ln(A_T C_e) \quad (5)$$

where R is the universal gas constant ($\text{J}\cdot\text{mol}^{-1}\text{K}^{-1}$), T is the temperature at 298K, b_T is the Temkin isotherm constant, A_T is the Temkin isotherm equilibrium binding constant ($\text{L}\cdot\text{g}^{-1}$).

The Dubinin-Radushkevich adsorption isotherm is used to express the mechanism of adsorption using the Gaussian energy distribution onto a heterogeneous surface (Dabrowski 2001). This model best fit to high solute activities and intermediate range of concentration data Eq. (6).

$$q_e = (q_s) \exp(-K_{ad} \varepsilon^2) \quad (6)$$

where q_e are the amount of adsorbate in the adsorbent at equilibrium ($\text{mg}\cdot\text{g}^{-1}$), q_s is the isotherm theoretical saturation capacity ($\text{mg}\cdot\text{g}^{-1}$), K_{ad} is Dubinin-Radushkevich isotherm constant ($\text{mol}^2\cdot\text{kJ}^2$) is related to the mean free energy of adsorption per mole of adsorbate, E in every molecule of adsorbate (for eliminating a molecule from its position in the sorption space to the infinity) can be calculated by the relationship (Foo and Hameed 2010) in Eq. (7).

$$E = \left[\frac{1}{\sqrt{2B_{DR}}} \right] \quad (7)$$

where B_{DR} is the isotherm constant, whereas the ε can be calculated in Eq. (8):

$$\varepsilon = RT \ln \left[1 + \frac{1}{C_e} \right] \quad (8)$$

where C_e , is the adsorbate equilibrium concentration ($\text{mg}\cdot\text{L}^{-1}$). This isotherm model has a unique temperature-dependent features that when an adsorption data at different temperatures are plotted as a function of logarithm of amount adsorbed ($\ln q_e$) against (ε^2) the square of potential energy, all appropriate data fall on the same curve, the characteristic curve (Dada *et al.* 2012).

The Temkin isotherm ($R^2=0.978$) best describes the experimental data (Fig. 2). This indicates that the Temkin isotherm best fit in describing the adsorption of RY 145 onto CPAC. This favors with the adsorption capacity produced by the Temkin isotherm ($q_{e,\text{pred}}$). The sorption process that follows the Temkin model involved the heat of sorption of particles in the outer layer. As dye molecules and binding sites interact, a linear decreased in the heat of sorption of all molecules in this layer happens as the binding energies of these molecules become uniformly

distributed up to a maximum binding energy (Igwe and Abia 2007; Vieira *et al.* 2011).

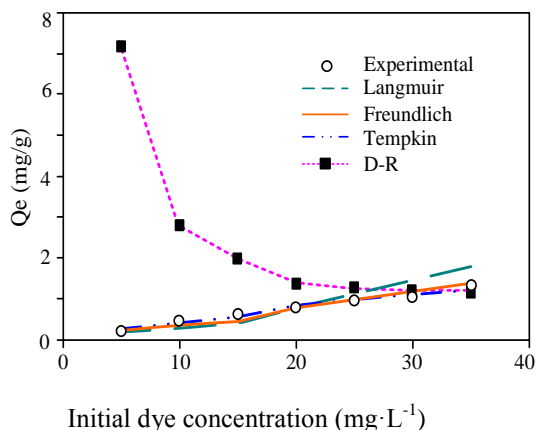


Fig. 2. Comparison of adsorption capacities of the isotherm models and actual experiment.

3.5 Adsorption kinetic studies

The linearized forms of the pseudo-first order, pseudo-second order kinetic models (Eq. 9-10) were employed to describe dye sorption data. Parameters q_e ($\text{mg}\cdot\text{g}^{-1}$) and q_t ($\text{mg}\cdot\text{g}^{-1}$) referred to the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium and to the amount of adsorbate adsorbed at contact time t , respectively. Rate constants k_1 (min^{-1}) and k_2 ($\text{g}\cdot\text{mg}^{-1}\text{min}^{-1}$) correspond to pseudo-first order and pseudo-second order adsorption, respectively.

Pseudo-first order equation:

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

Pseudo-second order equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (10)$$

Fitting the data to these equations, the pseudo-second order kinetic model represented the highest correlation ($R^2=0.999$) with the sorption data. At this point, the equilibrium sorption capacity of the pseudo-second order kinetic model ($0.722 \text{ mg}\cdot\text{g}^{-1}$) almost coincided with the optimized sorption capacity ($0.731 \text{ mg}\cdot\text{g}^{-1}$). This indicates that the chemisorption is the rate-controlling step in the sorption process that best describe the applicability of the experimental data for pseudo-second order model (Chowdury *et al.* 2011). Chemisorption was observed in various sorption studies on dyes and agricultural wastes (Sepulveda *et al.* 2004; Crini and Peindy 2006; Ncibi *et al.* 2008).

4. Conclusion

This study produced an activated carbon from the waste cocoa pods by chemical and physical activation. The produced biosorbents were applied to remove RY 145 dye from aqueous solution. The effects of the operating parameters on the dye removal were investigated in terms of adsorbent dose, initial dye concentration and contact

time. The optimum parameter conditions generated by the model were $17.5 \text{ mg}\cdot\text{L}^{-1}$ initial RY 145 concentration, 1.0 g of CPAC dosage, and 1.0 h contact time resulting to $0.7311 \text{ mg}\cdot\text{g}^{-1}$ adsorption capacity. The Temkin and Freundlich isotherms with $R^2=0.978$ and 0.933 fittingly described the experimental data. Whereas the pseudo second-order ($R^2=0.999$) equation best described the sorption process. These results implied that the chemisorption process is the rate limiting step. This study validated the application of indigenous waste material from an agricultural wastes as low-cost alternatives to commercially adsorbent materials.

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