

APPLICATION OF CARBONIZED MANGOSTEEN PEEL AS LOW-COST BIOSORBENT IN REMOVING HAIR DYE FROM AQUEOUS SOLUTION

Ratiwun Suwattanamala¹, Aimorn Prachuabmorn¹, Pornpun Watcharaviton² and Akapong Suwattanamala^{3,*}

Received: May 30, 2021; Revised: July 31, 2021; Accepted: August 25, 2021

Abstract

Mangosteen peel from agricultural waste was treated with concentrated sulphuric acid, resulting in a carbonized mangosteen peel powder (CMPP). It was applied as a biosorbent to adsorb hair dye from an aqueous solution. The biosorbent was characterized by Scanning electron microscopy (SEM), Brunauer-Emmet-Teller (BET) analysis, and Fourier-transform-infrared (FT-IR) spectroscopy. Batch adsorption experiments were performed to evaluate the effects of adsorbent dosage, contact time, and initial pH on the adsorption capacity and the percentage of hair dye removal. Optimal conditions for hair dye decolorization were 90 min of contact time, 0.25 g biosorbent in 50 ml of aqueous solution, and initial pH of 7.69. With these conditions, the adsorption capacity (q_e) was 25.25 mg/g, and the percentage removal of hair dye was 72.14%. The experimental data were demonstrated to well follow the presumption of the Freundlich isotherm and pseudo-second order kinetic models. The findings show that carbonized mangosteen peel can be utilized as a low-cost biosorbent for hair dye removal in aqueous solution.

Keywords: Hair dye, Mangosteen peel, Biosorption, Removing

Introduction

Hair dyes are widely used cosmetic products to cover graying hair or to alter hair color for fashion. Historically, hair dyeing has been employed since ancient Egyptian times, using natural products (Da França *et al.*, 2015). In modern times, it has become a common practice in both men and women of various ages. For example, it was estimated that 64% of French women in the age range 15-70 years used hair dye (Bernard *et al.*, 2016). The increasing

use of hair dye has resulted in the growth of the hair dye market. In 2019, the global hair color market produced revenues of 30.3 billion U.S. dollars (Ridder, 2020a), up from 11.4 billion U.S. dollars in 2017 (Ridder, 2020b). Synthetic hair dyes can be classified into four categories based on their color persistence: (1) temporary, (2) semi-permanent, (3) demi-permanent, and (4) permanent (Sankar *et al.*, 2017). Permanent hair dye is popular due to its

¹ Department of Environmental Health, Faculty of Public Health, Burapha University, Chonburi, Thailand.

² School of Occupational Health, Institute of Public Health, Suranaree University of Technology, Nakornrachasima, Thailand.

³ Department of Chemistry, Faculty of Sciences, Burapha University, Chonburi, Thailand. Tel. (66)-38-103112, Fax. (66)-38-103112, E-mail: akapong@buu.ac.th

* Corresponding author

stability (Mait *et al.*, 2017). The main components in this dye consist of primary intermediates, developer, and coupling agents. Phenylenediamines (PDs) and their derivatives such as *p*-phenylenediamine and *p*-aminophenol are commonly applied as the primary intermediates (Park *et al.*, 2018). The color of permanent hair dye is developed through the oxidation process, thus it is also known as oxidative hair dye. The primary intermediates are oxidized by the developer (or oxidizing agent), then the active intermediates react rapidly with the coupling agents and induce color formation (Morel and Christie, 2011). Various studies have indicated that *p*-phenylenediamine can cause allergic contact dermatitis (ACD) (Ortiz-Salvador *et al.*, 2017; Goebel *et al.*, 2018; Ko *et al.*, 2019). Several epidemiological studies have revealed the association between skin irritation and permanent hair dye exposure among consumers and hairdressers (Helaskosk *et al.*, 2014; Ortiz-Salvador *et al.*, 2017; Goebel *et al.*, 2018). Some authors reported adverse reactions resulting from the use of hair dye, i.e., damaged hair surface, headache, prickling sensation, urticaria, and rhinitis (Patel *et al.*, 2013; Helaskosk *et al.*, 2014; Tang *et al.*, 2016). These reviews suggest that some hair dyes can affect human health. The users should apply these products with caution to avoid harmful effects, especially hairdressers and cosmeticians who may have occupational health impacts due to the long-term exposure to allergens in hair dye.

During the hair dyeing process, some primary intermediates such as *p*-phenylenediamine (PPD) and *p*-toluenediamine (PTD) can be oxidized to new chemical compounds with high toxicity (Zanoni *et al.*, 2015). Small quantities of hair dye are bonded to the hair cortex (Mait *et al.*, 2017), while the excess chemical components are rinsed out with water and drained as salon wastewater. If untreated salon wastewater is released into the environment, it can cause impairment of the ecosystem. For example, it was reported that *p*-phenylenediamine can be converted to more toxic metabolites by microbes, and then have negative impacts on plant growth (Mishra *et al.*, 2020). Another study found potential adverse morphological and physiological effects of hair dye on zebrafish (*Danio rerio*) embryos, including mortality, changes in cardiac function, yolk stalk length, and DNA damage (Manjunatha *et al.*, 2020). Furthermore, hair dye contained in wastewater can deteriorate the aesthetic appearance of receiving waters, as well as diminish sunlight penetration and reduce photosynthesis, resulting in low dissolved oxygen levels (Mitrogiannis *et al.*, 2015). Therefore, the elimination of hair dye contaminants from the effluent is necessary for human health and

environmental protection. Adsorption is an effective method for removing synthetic dyes (Yagub *et al.*, 2014; Choi and Yu, 2019), including hair dye components (Saheed *et al.*, 2016). Activated carbon is usually utilized as an adsorbent due to its high efficiency. However, commercially available activated carbon is expensive; thus, if an inexpensive material was developed for the treatment of hair dye, it would reduce treatment costs. Mangosteen (*Garcinia Mangostana* L.) is a delicious tropical fruit that is commonly cultivated in Southeast Asia. The peel represents approximately 60% of the whole fruit (Mohammed *et al.*, 2014), and is generally discarded as agricultural waste. Hence, it may be a suitable raw material to produce low-cost biosorbent. Previous investigations confirmed that adsorbents derived from mangosteen peel were able for eliminating water contaminants from water, such as heavy metal and synthetic dyes (Ahmad and Alrozi, 2010; Huang *et al.*, 2014). However, no information has been studied on application for hair dye removal. In this study, a biosorbent was prepared from mangosteen peel via simple carbonization with sulphuric acid. Then, it was tested for decolorization of hair dye. The objective of this research is to evaluate the efficiency of the carbonized mangosteen peel biosorbent in removing permanent hair dye from an aqueous solution.

Materials and Methods

Adsorbate

A permanent (oxidative) hair dye of natural black shade was used in the experiments. It was selected and purchased from a convenience store. The hair dye product consisted of color shampoo and conditioning developer; chemically, it contained various compounds such as *p*-phenylenediamine (PPD), resorcinol, and hydrogen peroxide. A stock hair dye solution of 1000 mg/L was obtained by dissolving the required proportion of color shampoo and developer in distilled water. Then, different concentrations were produced by dilution for further experiments. The initial and residual dye concentrations were detected with a visible spectrophotometer (Hach model DR2700, USA) at a maximum wavelength of 410 nm.

Biosorbent

Mangosteen peel used in the experiments was obtained from a local market in the eastern region of Thailand. The peel was dried under sunlight to reduce moisture content until a constant weight was gained. The peels were then ground to produce a fine powder and stored in a glass jar with airtight

lid until further use. The carbonized mangosteen peel powder (CMPP) was prepared based on a procedure reported by Huang *et al.* (2014). Fifty grams of dried granulated mangosteen peel was reacted with 50 mL concentrated sulfuric acid (98%), then kept at $28 \pm 2^\circ\text{C}$ for 24 h. The resulting black residue was neutralized by sodium hydroxide solution. This wet slurry was placed on a Whatman No. 1 filter paper to facilitate drainage water and collect the residue, which was then reconditioned in 1 M sulfuric acid solution. After 30 min of magnetic stirring, the treated product was separated by filtration and gradually rinsed with hot distilled water until the filtrate attained a neutral pH. The wet filtered cake was left to dry in a hot air oven at 60°C for 12 h, then crushed and sieved to obtain a fine particle size of 250-500 μm . Then CMPP was stored in an airtight bottle for further use as biosorbent.

Characterization of Biosorbent

Surface morphological observation of the CMPP was recorded by scanning electron microscopy (SEM; LEO 1450 VP). The specific surface area was examined by the Brunauer, Emmet, and Teller method (BET; BELSORP-mini-28SP instrument). Functional groups on surface of the biosorbent were characterized using a Fourier-transform-infrared (FT-IR) spectrometer (Perkins Elmer, model Spectrum One) in the wavelength range of 400-4000 cm^{-1} .

The point of zero charge (pH_{pzc}) of the biosorbent was evaluated by the pH drift method (Panumati *et al.*, 2008). A series of Erlenmeyer flasks containing 50 mL of 0.1 M NaCl was prepared with initial pH values ranging from 2 to 12, using either 0.1M HCl or 0.1 M NaOH. A 0.15 g sample of CMPP was added to each aliquot and agitated for 24 h at room temperature. The final pH value of the filtrate was measured by pH meter (Hach, model HQ 11d). The pH_{pzc} is the point at which the difference of initial and final pH value is equal to zero.

Batch adsorption experiments

Batch adsorption experiments were performed in a set of 125 mL conical flasks containing 50 mL of oxidative hair dye solution with an initial concentration of 150 mg/L and a known amount of adsorbent. This initial dye concentration was selected with reference on the color containing in real hair dye wastewater. The mixture flasks were agitated at speed of 120 rpm at room temperature. The effects of adsorbent dosage (0.05-1 g), contact time (0-180 min), dye concentration (25-200 mg/L), and initial pH (2-11) were studied. After adsorption, the CMPP was separated by filtration and residual dye in the supernatant solution was investigated for adsorption efficiency. The percentage of hair dye removal (Removal%) and the adsorption capacity of

adsorbents at equilibrium, q_e (mg/g) were calculated from formulas (1) and (2), respectively (Onrassami *et al.*, 2017).

$$\text{Removal \%} = \left(\frac{C_i - C_e}{C_e} \right) \times 100 \quad (1)$$

$$q_e = \frac{(C_i - C_e) \times V}{W} \quad (2)$$

where C_i and C_e (mg/L) are the initial and equilibrium concentrations of hair dye in solution, V is the volume of hair dye solution (L) and W is the weight of dried adsorbent (g).

Results and Discussion

Characterization of Biosorbent

Surface morphology of the CMPP was examined at 500x magnification. Cavernous, porous and rough structures were observed on the surface of biosorbent (Figure 1a), which could encourage the adsorption of dye molecules. The coverage with dye molecules on surface of CMPP was observed after hair dye adsorption (Figure 1b).

The specific surface area and average pore diameter of the CMPP were determined to be 1.34 m^2/g and 2.19 nm, respectively. The CMPP was categorized in the mesopore region following to the IUPAC classification; in this system, pores are

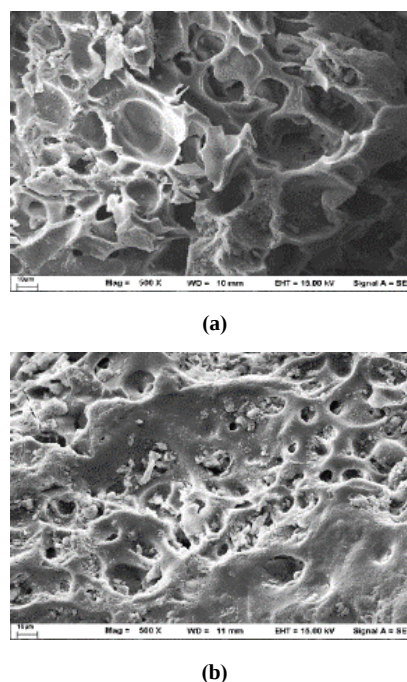


Figure 1. SEM image of (a) CMPP, and (b) CMPP after hair dye adsorption.

classified as micropores (<2 nm diameter), mesopores (2-50 nm diameter) or macropores (>50 nm diameter) (Sánchez-Martín *et al.*, 2011). The prevalence of mesopores on the CMPP surface may facilitate dye adsorption (Marković *et al.*, 2015).

The FTIR spectrum of CMPP is illustrated in Figure 2. It indicates the presence of various functional groups. The broad peak around 3201 cm^{-1} corresponds to the O-H stretching vibration, showing the presence of hydrogen-bonded OH groups in the biosorbent (Wang *et al.*, 2019). The peak at 2919 cm^{-1} can be assigned to the C-H stretching of methyl, methylene, and methoxy groups (Inyinbor *et al.*, 2016). The peak presenting around 1704 cm^{-1} is caused by C=O stretching of carbonyl groups (Peláez-Cid *et al.*, 2016). The peak around 1600 cm^{-1} corresponds to C=C stretching vibration. The peak occurring at 1432 cm^{-1} indicates to the C=C stretching of aromatic rings (Royer *et al.*, 2009). The peaks presenting between 1158 cm^{-1} and 1111 cm^{-1} are attributed to the C-O stretching vibration in carboxyl acids, alcohols, phenols and esters (Patawat *et al.*, 2020). The peak appearing at 1032 cm^{-1} may belongs to C-O bonding of phenols (Royer *et al.*, 2009). These results suggest that the CMPP contains functional groups that are favorable for adsorbing hair dye molecules.

The pH_{pzc} of the CMPP was found at pH 2.16. It implies that the surface of the biosorbent is a strong acid (Peláez-Cid *et al.*, 2016). When the pH value of aqueous solution is lower than the pH_{pzc} , the surface of the biosorbent becomes positively charged, while in a solution with pH higher than the pH_{pzc} , the surface of the biosorbent is negatively charged (Marković *et al.*, 2015; Peláez-Cid *et al.*, 2016).

In this study, dark brown color product obtained from the oxidation of *p*-phenylenediamine (PPD), resorcinol, and hydrogen peroxide mixtures under alkaline condition. The brown color compound is known as a formation of polyindophenol. Its proposed structure is adapted from Bessegato *et al.* (2018) and shown in Figure 3.

Proposed adsorption mechanism of polyindophenol (brown hair dye) onto CMPP was illustrated in Figure 3. The occurrence of hydroxyl (-OH) and carbonyl (-C=O) groups on the CMPP surface in FTIR spectrum (as shown in Figure 2) potentially contributes to interact with polyindophenol (brown hair dye). Hydrogen bonding between hydrogen atoms in hydroxyl groups of the CMPP adsorbent and nitrogen atoms in amine groups of polyindophenol seems to play an important role in adsorption mechanism as proposed in Figure 3. Moreover, the ion dipole force between positive charged iminium groups of polyindophenol

in acidic or neutral medium and partially negative charges on oxygen atoms in carbonyl groups might also be formed during on adsorption process.

Effect of biosorbent dosage

The biosorbent dosage affecting on efficiency of hair dye adsorption was evaluated using 0.05, 0.25, 0.50, 0.75, and 1.0 g of CMPP in 50 mL of aqueous solution. The hair dye concentration was 150 mg/L for all batch experiments. The highest efficiency of hair dye removal (71.11%) was at the biosorbent dosage of 0.25 g, with q_e of 21.33 mg/g. Thus, this optimal CMPP dosage was used for all further experiments. Increases in biosorbent dosage resulted in decreases in both q_e and percentage of dye removal (Figure 4). This could be owing to obstruction of active sites as resulting from the aggregation of biosorbent particles (Inyinbor *et al.*, 2016).

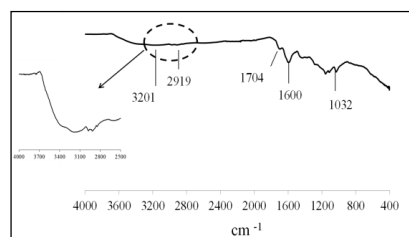


Figure 2. FTIR spectrum of CMPP.

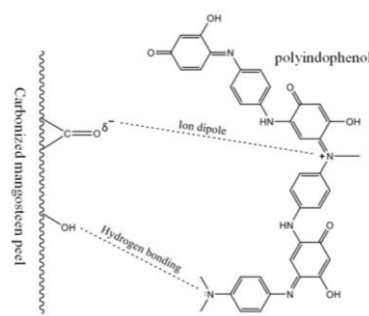


Figure 3. Proposed adsorption mechanism of hair dye on CMPP.

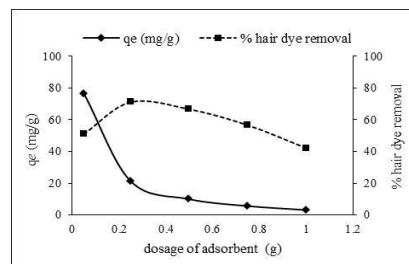


Figure 4. Effect of biosorbent dosage on adsorption of hair dye.

Effect of contact time

A set of different contact time ranging from 5 to 180 min was conducted in this experiment. The effect of contact time on hair dye adsorption onto the CMPP is illustrated in Figure 5. The percentage of hair dye removal increased with longer contact time. It was found that nearly 68% removal of hair dye occurred within 90 min; with greater contact time, dye removal increased only slightly. The adsorption capacity also showed a similar trend, with an increase from 12.33 mg/g to 20.33 mg/g with an increase in the contact time from 5 to 90 min, but with little or no gain for longer contact time. These findings could be elucidated by the availability of more binding sites on the CMPP initially, and as the available binding sites became occupied with hair dye molecules, the rate of adsorption became slower until a point of equilibrium (Dahri *et al.*, 2015). In this case, the equilibrium was reached at around 90 min, and thus was selected as sufficient contact time for later experiments.

Effect of initial pH

The value of pH in aqueous solution can influence the surface charges of the biosorbent and the chemistry of adsorbate (Wang *et al.*, 2019). This experimental section was done over the pH range from 1.5 to 11, including the ambient pH of 7.6. The results are illustrated in Figure 6. The percentage of hair dye removal and the adsorption capacity slightly increased with increasing pH value from 1.5 to 5, then gradually decreased from pH 5 to 7.6. These results were not significant different, indicating the pH range of 1.5-7.6 has little effect on hair dye adsorption. This phenomenon disagreed with pH_{pzc} concept. It suggests that the electrostatic interaction is not a dominant role of interaction between the surface charges of CMPP and the hair dye molecules. Considering, some surface functional groups of CMPP, such as carbonyl and hydroxyl groups can also contribute to hair dye adsorption process through ion dipole interaction and hydrogen bonding. This is compatible with the result of other researcher (Dahri *et al.*, 2015). Sharp decreases in the adsorption efficiency were observed when the pH solution was raised to 9 and 11. Moreover, the aqueous solution became turbid at pH 11. It is possible that strongly alkaline medium can react with chemical compounds of hair dye to promote suspended particles.

The highest percentage removal (78%) was obtained at pH 5, with adsorption capacity of 27.50 mg/g. However, the removal efficiency and the adsorption capacity at the ambient pH (7.6) were only minimally different than at pH 5, and thus

ambient pH was selected for the remaining experiments.

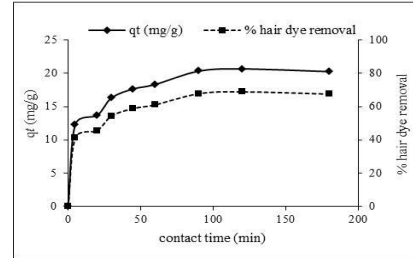


Figure 5. Effect of contact time on adsorption of hair dye.

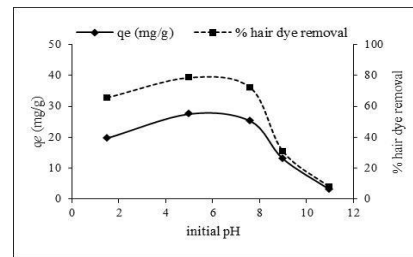


Figure 6. Effect of initial pH on adsorption of hair dye.

Equilibrium Adsorption Isotherms

The isotherm study was tested to explain the adsorption behavior of the CMPP to remove the hair dye from aqueous solution. Two widely known models, Langmuir and Freundlich isotherm plots were employed in the present study. The Langmuir plot infers a monolayer adsorption onto the surface of adsorbent, while the Freundlich model depicts a multilayer adsorption (Yagub *et al.*, 2014).

The linear Langmuir model equation is as follows (Dahri *et al.*, 2015)

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (3)$$

The dimensionless constant separation factor (R_L) is a determined by the mathematical equation:

$$R_L = \frac{1}{1+bC_i} \quad (4)$$

where C_e is the dye equilibrium concentration (mg/L), q_e is the equilibrium adsorption capacity (mg/g), q_m is the maximum monolayer adsorption capacity (mg/g) and b is the Langmuir constant (L/mg). R_L value reveals the type of Langmuir isotherm that is unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$).

The linear Freundlich model equation is given as follows (Etim *et al.*, 2016):

$$\log q_e = \log K_F + (1/n) \log C_e \quad (5)$$

where K_F is the Freundlich constant reflected by adsorption capacity (L/mg) and n is the constant related to adsorption intensity. Generally, if $n=1$, the adsorption is linear; if $n>1$, the adsorption is a physical process; if $n<1$, the adsorption is a chemical process (Marković *et al.*, 2015).

The results acquired from the Langmuir and Freundlich models for the elimination of hair dye from solution and onto the CMPP are presented in Figure 7. The experimental data of Langmuir adsorption parameters resulted in negative slopes and intercepts, which imply that the adsorption behavior does not meet the assumptions of the Langmuir approach. On the other hand, the experimental data fit well to the Freundlich model ($R^2=0.96$), which suggests multilayer adsorption and implies a heterogeneous surface of the CMPP.

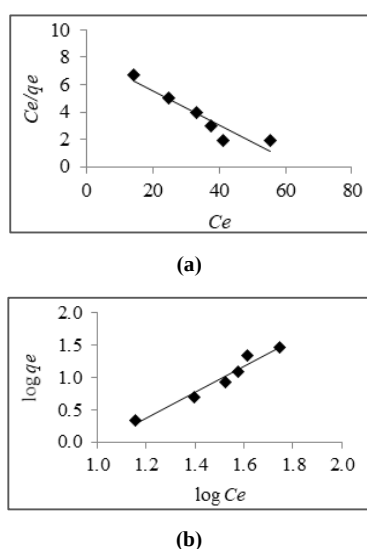


Figure 7. Adsorption isotherms for hair dye removal using CMPP (a) Langmuir isotherm plot; (b) Freundlich isotherm plot.

Table 1. Adsorption parameters of Langmuir and Freundlich isotherm models for hair dye removal using CMPP.

	CMPP
Langmuir isotherm	
q_m (mg/g)	-7.99
b (L/mg)	0.02
R^2	0.88
Freundlich isotherm	
K_F (L/ mg)	0.01
n	0.5
R^2	0.96

The data also demonstrated a small value of n , indicating that the biosorption of hair dye onto the CMPP is a chemical process (Choi and Yu, 2019). The adsorption parameter data are summarized in Table 1.

Adsorption Kinetics

The kinetic studies of hair dye onto carbonized mangosteen peel were evaluated by time-dependent studies. Two distinguished kinetic models, namely pseudo-first-order and pseudo-second-order were utilized to understand the dynamics of adsorption of hair dye onto CMPP. The pseudo-first-order model uses to describe the physical interactions between the adsorbate and adsorbent molecules, whereas the pseudo-second-order model explains chemical interactions between the two components (Sharma *et al.*, 2018). The two equations can be expressed, respectively, as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

where q_e (mg/g) and q_t (mg/g) are the adsorption capacity at equilibrium and contact time t (min), respectively; k_1 is the pseudo-first-order rate constant (min^{-1}); and k_2 is the pseudo-second-order rate constant (g/mg min). The kinetic parameters of both pseudo-first-order and pseudo-second-order models were determined simultaneously by equations (6) and (7), with results summarized in Table 2. To obtain the more appropriate model, the experimental adsorption data were fitted to the linear plot of kinetic models showing the strength relationship resulting in greater value of correlation coefficient (R^2). A linear plot of t/q_t versus t , illustrates good agreement between the experimental adsorption capacity values and the theoretical adsorption capacity obtained from the pseudo-second-order model; also, the pseudo-second-order model provides better R^2 than the pseudo-first-order model, as reported in Table 2.

Table 2. Kinetic parameters obtained from pseudo-first and pseudo-second-order models for the adsorption process of hair dye onto CMPP.

Model	Parameters	
pseudo-first-order	q_e (mg/g)	9.714
	k_1 (min^{-1})	0.027
	R^2	0.968
pseudo-second-order	q_e (mg/g)	21.413
	k_2 (g/mg min)	0.006
	R^2	0.997
experimental data	q_e (mg/g)	20.334

This indicates that the kinetics of the adsorption process can be more suitably described by chemical adsorption mechanisms between adsorbate and adsorbent. Electron sharing or electron transfer under the experimental conditions might be rate controlling factors (He *et al.*, 2017; Choi and Yu, 2019).

Conclusions

A locally available mangosteen peel waste was modified to CMPP biosorbent by a non-poisonous and simple carbonization process with concentrated sulphuric acid. The characterization of CMPP revealed a heterogenous surface containing various functional groups that could interact with adsorbate molecules such as in oxidative hair dye. The removal efficiency and the adsorption capacity of hair dye from aqueous medium onto the CMPP were investigated in batch experiments. The percentage of hair dye removal and the adsorption capacity depended on biosorbent dosage, contact time and initial pH. The Freundlich isotherm described the adsorption process very well. A pseudo-second-order kinetic model explained the experimental adsorption data. The findings of this study suggest that CMPP could be possibly promoted as an environmental friendly and low-cost biosorbent for hair dye elimination in aqueous solution.

Acknowledgements

We are grateful to the Faculty of Public Health, Burapha University for financial support. We are also thankful to the Faculty of Science, Burapha University for the laboratory facilities. The assistance from the Institute of Public Health, Suranaree University of Technology is also appreciated.

References

- Ahmad, M.A. and Alrozi, R. (2010). Optimization of preparation conditions for mangosteen peel-based activated carbons for the removal of Remazol Brilliant Blue R using response surface methodology. *Chem. Eng. J.*, 165(3):883-890.
- Bernard, A., Houssin, A., Ficheux, A.S., Wesolek, N., Nedelec, A.S., Bourgeois, P., Hornez, N., Batardiere, A., Misery, L., and Roudot, A.C. (2016). Consumption of hair dye products by the French women population: Usage pattern and exposure assessment. *Food Chem. Toxicol.*, 88:123-132.
- Bessegato, G.G., Souza, J.C., Cardoso, J.C., and Zanoni, M.V.B. (2018). Assessment of several advanced oxidation processes applied in the treatment of environmental concern constituents from a real hair dye wastewater. *J. Environ. Chem. Eng.*, (6):2,794-2,802.
- Choi, H.J. and Yu, S.W. (2019). Biosorption of methylene blue from aqueous solution by agricultural bioadsorbent corn cob. *Environ. Eng. Res.*, 24(1):99-106.
- Da França, S.A., Dario, M.F., Esteves, V.B., Baby, A.R., and Velasco, M.V.R. (2015). Types of hair dye and their mechanisms of action. *Cosmetics*, 2:110-126.
- Dahri, M.K., Kook, M.R.R., and Lim, L.B.L. (2015). Application of *Casuarina equisetifolia* needle for the removal of methylene blue and malachite green dyes from aqueous solution. *Alex. Eng. J.*, 54:1,253-1,263.
- Etim, U.J., Umoren, S.A., and Eduok, U.M. (2016). Coconut coir dust as a low cost adsorbent for the removal of cationic dye from aqueous solution. *J. Saudi Chem. Soc.*, 20:S67-S76.
- Goebel, C., Diepgen, T.L., Blömeke, B., Gaspari, A.A., Schnuch, A., Fuchs, A., Schlotmann, K., Krasteva, M., and Kimber, I. (2018). Skin sensitization quantitative risk assessment for occupational exposure of hairdressers to hair dye ingredients. *Regul. Toxicol. Pharmacol.*, 95:124-132.
- He, H., Gan, Q., and Feng, C. (2017). Preparation and application of Ni(II) ion-imprinted silica gel polymer for selective separation of Ni(II) from aqueous solution. *RSC Adv.*, 7:15,102-15,111.
- Helaskoski, E., Suojalehto, H., Virtanen, H., Airaksinen, L., Kuuliala, O., Aalto-Korte, K., and Pesonen, M. (2014). Occupational asthma, rhinitis, and contact urticaria caused by oxidative hair dyes in hairdressers. *Ann. Allergy Asthma Immunol.*, 112(1):46-52.
- Huang, K., Xiu, Y., and Zhu, H. (2014). Removal of hexavalent chromium from aqueous solution by crosslinked mangosteen peel biosorbent. *Int. J. Environ. Sci. Technol.*, 12:2,485-2,492.
- Inyinbor, A.A., Adekola, F.A., and Olatunji, G.A. (2016). Kinetics, isotherms and thermodynamic modeling of liquid phase adsorption of Rhodamine B dye onto *Raphia hookeri* fruit epicarp. *Water Resour. Ind.*, 15:14-27.
- Ko, H.-Y., Lin, Y.-H., Shih, C.-J., and Chen, Y.-L. (2019). Determination of phenylenediamines in hair colors derivatized with 5-(4,6-dichlorotriazinyl) aminofluorescein via micellar electrokinetic chromatography. *J. Food Drug Anal.*, 27:825-831.
- Mait, S., Sinha, S.S., and Sing, M. (2017). Microbial decolorization and detoxification of emerging environmental pollutant: cosmetic hair dyes. *J. Hazard. Mater.*, 338:356-363.
- Manjunatha, B., Han, L., Kundapur, R.R., Liu, K., and Lee, S.J. (2020). Herbul black henna (hair dye) causes cardiovascular defects in zebrafish (*Danio rerio*) embryo model. *Environ. Sci. Pollut. Res.*, 27:14,150-14,159.
- Marković, S., Stankovic, A., Lopicic, Z., Lazarevic, S., Stojanovic, M., and Uskokovic, D. (2015). Application of raw peach shell particles for removal of methylene blue. *J. Environ. Chem. Eng.*, 3:716-724.
- Mishra, V., Sharma, U., Rawat, D., Benson, D., Singh, M., and Sharma, R.S. (2020). Fast-changing life-styles and ecotoxicity of hair dyes drive the emergence of hidden toxicants threatening environmental sustainability in Asia. *Environ. Res.*, 184:109,253.
- Mitrogiannis D., Markou G., Çelekli A., and Bozkurt H. (2015). Biosorption of methylene blue onto *Arthrospira platensis* biomass: Kinetic, equilibrium and thermodynamic studies. *J. Environ. ChEm Eng.* 2015., 3:670-680.
- Mohammed, M.A., Shitu, A., Tadda, M.A., and Ngabura, M. (2014). Utilization of various agricultural waste materials in the treatment of industrial wastewater containing heavy metals: A review. *Int. Res. J. Environ. Sci.*, 3(3):62-71.
- Morel, O.J.X. and Christie, R.M. (2011). Current trends in the chemistry of permanent hair dyeing. *Chem. Rev.*, 111(4):2,537-2,561.

- Onrassami, R., Suwattanamala, A., Kaewkrajang, A., and Prachuabmorn, A. (2017). Utilization of powdered activated carbon as adsorbent for dye removal from treated textile wastewater. In : Proceedings of the 4th Asia-Pacific Conference on Engineering and Applied Science, August 27-29, 2017, Bali, Indonesia, p. 91-98.
- Ortiz-Salvador, J.M., Esteve Martínez, A., Subiabre Ferrer, D., Victoria Martínez, A.M., de la Cuadra Oyanguren, J., and Zaragoza Ninet, V. (2017). Para-phenylenediamine allergic contact dermatitis due to henna tattoos in a child and adolescent population. *An Pediatr (Barc.)*, 86(3):122-126.
- Panumati, S., Chudecha, K., Vankhaew, P., Choolert, V., Chuenchom, L., Innajitara, W., and Sirichote, O. (2008). Adsorption of phenol from diluted aqueous solutions by activated carbons obtained from bagasse, oil palm shell and pericarp of rubber fruit. *Songklanakarin J. Sci. Technol.*, 30(2):185-189.
- Park, H., Hwang, J.-h., Han, J.-S., Lee, B.-S., Kim, Y.-B., Joo, K.-M., Choi, M.-S., Cho, S.-A., Kim, B.-H., and Lim, K.-M. (2018). Skin irritation and sensitization potential of oxidative hair dye substances evaluated with in vitro, in chemico and in silico test methods. *Food Chem. Toxicol.*, 121:360-366.
- Patawat, C., Silakate, K., Chuan-Udom, S., Supanchaiyamat, N., Hunt, A. J., and Ngernyen, Y. (2020). Preparation of activated carbon from *Dipterocarpus alatus* fruit and its application for methylene blue adsorption. *RSC Adv.*, 10:21,082-21,091.
- Patel, D., Narayana, S., and Krishnaswamy, B. (2013). Trends in use of hair Dye: a cross-sectional study. *Int. J. Trichology*, 5:140-143.
- Peláez-Cid, A.A., Herrera-González, A.M., Salazar-Villanueva, M., and Bautista-Hernández, A. (2016). Elimination of textile dyes using activated carbons prepared from vegetable residues and their characterization. *J. Environ. Manage.*, 181(1):269-278.
- Ridder, M. (2020a). Global hair colorants market size 2019 & 2025. Available from: <https://www.statista.com/statistics/275740/us-households-usage-of-hair-coloring-products/> Accessed date: Nov 23, 2020.
- Ridder, M. (2020b). Global hair colorants market retail value 2012- 2017. Available from: <https://www.statista.com/statistics/990518/global-hair-color-retail-sales-value>. Accessed date: Nov 23, 2020.
- Royer, B., Cardoso, N.F., Lima, E.C., Vaggetti, J.C.P., Simon, N.M., Calvete, T., and Veses, R.C. (2009). Applications of Brazilian pine- fruit shell in natural and carbonized forms as adsorbents to removal of methylene blue from aqueous solutions- Kinetic and equilibrium study. *J. Hazard. Mater.*, 164:1,213-1,222.
- Saheed, I. O., Adekola, F.A., and Olatunji, G.A. (2016). Adsorption of *p*-phenylenediamine onto activated carbon prepared from *Jatropha curcas* and *Terminalia catappa* seed coats. *Jordan J. Chem.*, 11(1):50-67.
- Sánchez- Martín, J., Beltrán- Heredia, J., and Gibello-Pérez, P. (2011). Adsorbent biopolymers from tannin extracts for water treatment. *Chem. Eng. J.*, 168:1,241-1,247.
- Sankar, J., Sawarkar, S., Malakar, J., Rawat, B.S., and Ali, M.A. (2017). Mechanism of hair dying and their safety aspects: A Review. *Asian J. Appl. Sci.*, 10(4):190-196.
- Sharma, G., Kumar, A., Naushad, M., García-Peñas, A., Al-Muhtaseb, A.H., Ghfar, A.A., Sharma, V., Ahamad, T., and Stadler, F.J. (2018). Fabrication and characterization of gum arabic- cl- poly (acrylamide) nanohydrogel for effective adsorption of crystal violet dye. *Carbohydr. Polym.*, 202:444-453.
- Tang, Y., Dyer, J.M., Deb-Choudhury, S., and Li, Q. (2016). Trace metal ions in hair from frequent hair dyers in China and the associated effects on photo-oxidative damage. *J. Photochem. Photobiol. B, Biol.*, 156:35-40.
- Wang, G., Chen, Y., Xu, G., and Pei, Y. (2019). Effective removing of methylene blue from aqueous solution by tannins immobilized on cellulose microfibers. *Int. J. Biol. Macromol.*, 129(19):198-206.
- Yagub, M.T., Sen, T.K., Afroze, S., and Ang, H.M. (2014). Dye and its removal from aqueous solution by adsorption: A review. *Adv. Colloid Interface Sci.*, 209:172-184.
- Zanoni, T.B., Hudari, F., Munnia, A., Peluso, M., Godschalk, R.W., Zanoni, M.V.B., den Harto, G.J.M., Bast, A., Barros, S.B.M, Maria-Engler, S.S., Hageman, G.J., and de Oliveira, D.P. (2015). The oxidation of *p*-phenylenediamine, an ingredient used for permanent hair dyeing purposes, leads to the formation of hydroxyl radicals: Oxidative stress and DNA damage in human immortalized keratinocytes. *Toxicol. Lett.*, 239:194-204.