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Comparative Study on Traditional Indigo Dyeing onto Cotton Fabric Using Ripe Banana and Sodium Dithionite as Reducing Agents

S. LASOPHA[1,*], R. WATANESK[2] and S. DEJMANEE[1]

[1]Department of Chemistry, School of Science, Walailak University, Nakhon Si Thammarat-80161, Thailand
[2]Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai-50200, Thailand

*Corresponding author: Fax: +66 42970029; Tel: +66 899416565; E-mail: sudkamon2009@hotmail.com; khim.2007@hotmail.com

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In most industrial and conventional dyeing processes, indigo dye reduced in a high alkaline which sodium dithionite is of major importance. However, the processes involve many economical, ecological and technical problems. In this study, sodium dithionite and also ripe banana were used as reducing agents for indigo dyeing onto cotton fabric. Their capability of indigo reduction and also their kinetic and thermodynamic studies of indigo dyeing were investigated using UV-visible spectroscopy at λ_{max} 410 nm. Results revealed that under the same reduction condition of pH-13, 30 °C, sodium dithionite exercised its superiority in terms of reducing time, the amount of reducing agent and yield of reduced indigo over ripe banana. In addition, the kinetic data evaluated *via* pseudo-second order model reveals that the activation energy of dyeing process using sodium dithionite as reducing agent was lower than the energy required to dye cotton fabric using ripe banana. Moreover, the adsorption studies of indigo dye on cotton fabric indicated that both reducing agents fitted well with the Langmuir model and their adsorption processes are exothermic and spontaneous. However, the cotton fabric dyeing using ripe banana as reducing agent gave lighter color measured in term of its lightness compared to using sodium dithionite.

Keywords: Indigo, Ripe banana, Reducing agents, Kinetic, Thermodynamic.

INTRODUCTION

Indigo dye is one of the natural dye extracted from plants which commonly used in local community in the northern-east of Thailand. It has a distinctive blue color, insoluble in water so that it has to be reduced into the water soluble leuco form before dyeing onto cotton fabric. In conventional indigo dyeing process, the indigo dye is reduced in a high alkaline (pH about 13) which sodium dithionite is of major importance[1]. It is considered environmentally unfavorable. Hence, attempts are being made to replace sodium dithionite by eco-friendly more attractive alternatives such as organic biodegradable[2-4], enzymes[5], catalytic hydrogenation and direct or indirect electrochemical reductive methods[6]. The addition, physical process employing ultrasound, magnetic field or UV applications have shown to be practical application enabling to solve ecological problems[7]. However, such compounds are expensive and it is not possible to use those techniques for traditional indigo dyeing process. The present work is aimed to utilize ripe banana as reducing agent in traditional indigo dyeing process which offer several advantages. Ripe banana contains reducing sugar in more quantities. It is available in all seasons, low cost and safety in use. Moreover, the by-products formed are nontoxic and biodegradable. In this paper, traditional indigo dyeing on cotton fabric using both ripe banana as a reducing agents is reported in comparable with the process of using sodium dithionite.The studies include their efficacy of reduction for indigo dyeing, the kinetic and thermodynamic data and the depth of shade of the dyed cotton in order to assess the possibility of the use of as ecofriendly alternative to sodium dithionite in the traditional indigo dyeing process.

EXPERIMENTAL

Ripe banana and cotton fabric were purchased from the local community in SakonNakhon, Thailand. Indigo dye were purchased from Sigma-Aldrich, Germany. Nitrogen gas was also purchased from the United Industrial Gas Ltd., Thailand. Sodium dithionite and sodium hydroxide were purchased from Ajax Finechem Pty, New Zealand. Distilled water was used through out the experiments.

A 100 g of cotton fabric sample was clean to remove the wax and impurities in a mixture of 7 g of soap flakes and 3 g of sodium carbonate in 2 L of water for 1 h at 100 °C. Repeated rinsing under distilled water was followed, the cotton fabrics were then dried in air[9].

Reduction of indigo dye by banana and sodium dithionite: A 40 g of ripe banana and 8 g sodium dithionite was added separately into a 100 mL of sodium hydroxide solution in 125 mL Erlenmeyer flask at pH of about 13. Each flask was capped with a one-hole rubber with N_2 gas blowing under magnetic stirring. After 10 min, 0.01 g of indigo dye was added into the solution. Then, the absorbance of leuco indigo in each supernatant solution was determined at various reducing time (0 to 72 h) at 30 °C using UV-visible spectrophotometer (UV mini 1240 V, Shimadzu, Japan) at 410 nm. Yield of the reduced indigo (leuco indigo) was calculated from a standard calibration curve based on absorbance *vs*. indigo dye concentration.

Indigo dyeing on cotton fabric

Batch kinetic study: The leuco indigo dye solution was prepared by reducing indigo dye with ripe banana and also with sodium dithionite separately at various initial dye concentrations. A 100 mL dye solution was filled in each 125 mL Erlenmeyer flask then placed in a water bath operated at various temperatures (30, 40, 50 and 60 °C) for 15 min. Then the pre-warmed cotton fabric in water bath, was immersed in the dye solution. The dyed fabric samples was rapidly withdrawn from the dyeing bath after soaking at various times (10 to 120 min). The leuco indigo concentrations were determined at initial and at subsequent interval of every 10 min from 10 to 60 min and every 30 min from 60 to 120 min using a standard calibration curve based on its absorbance at 410 nm *vs*. indigo dye concentration. The amount of dye adsorbed (mg/g cotton) at any time (q_t) was calculated using the relations: $q_t = (C_i\text{-}C_t)(V/m)$, where C_i and C_t are the indigo dye concentration (mg/L) at initial time and time t, respectively. mis the weight (g) of the cotton fabric and V is the volume (L) of the solution[8]. The mechanism of the adsorption of indigo dye on cotton fabric was also investigated at 30 °C based on the pseudo-second order equation, $1/q_t = 1/(k_2q_e^2) + (1/q_e)$ where q_t are the amounts of dye adsorbed at time t.

Batch equilibrium study: The adsorption isotherm of indigo dyeing on cotton fabric was investigated under the condition of an MLR of 1:100 and temperature (30, 40, 50 and 60 °C) in the initial indigo dye concentration range 6 to 220 mg/L. The experiments were carried out by immersing the cotton fabric sample into various concentrations of leuco indigo dye solutions in 125 mL Erlenmeyer flask in the water bath at various controlled temperature (30, 40, 50 and 60 °C). The leuco indigo concentrations were determined at initial and at equilibrium times. The amount of dye adsorbed (mg/g cotton), at equilibrium time was calculated as follows, $q_e = (C_i\text{-}C_e)(V/m)$, where C_i and C_e are the indigo dye concentration (mg/L) at initial time and equilibrium time, respectively[9,10].

Color measurement: Each dyed cotton fabric sample at the optimum condition was washed in distilled water until the rinsed water was neutral, then dried at room temperature. The color strength, tones (a^* and b^*) and light/darkness (L^*) were measured using CIELAB system (mini scan XE plus, hunter lab, USA).

RESULTS AND DISCUSSION

Reduction of indigo dye by ripe banana and sodium dithionite: The indigo dye was completely reduced separately to leuco indigo by the ripe banana and sodium dithionite to liquor at 40:100 and 8:100 w/v, within 12 h and 70 min, respectively (Fig. 1). Under the same reduction condition of indigo dye in sodium hydroxide solution at pH-13 at 30 °C, it can be observed that the use of sodium in reduction presented better values of reducing time, the amount of reducing agent and yield of reduced indigo than obtained when indigo was reduced by ripe banana (Fig. 2).

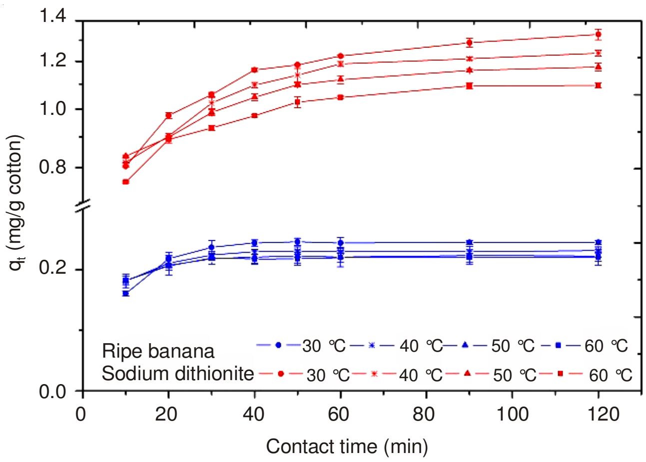

Fig. 2. Kinetic evaluations of contact time and temperature of indigo dyeing on cotton fabric using ripe banana and sodium dithionite as reducing agents at various temperatures

Indigo dyeing on cotton fabric

Batch kinetic study: From Fig. 2, the dye adsorption rate of both ripe banana and sodium dithionite rapidly increases within the first period, there after the adsorption tend to

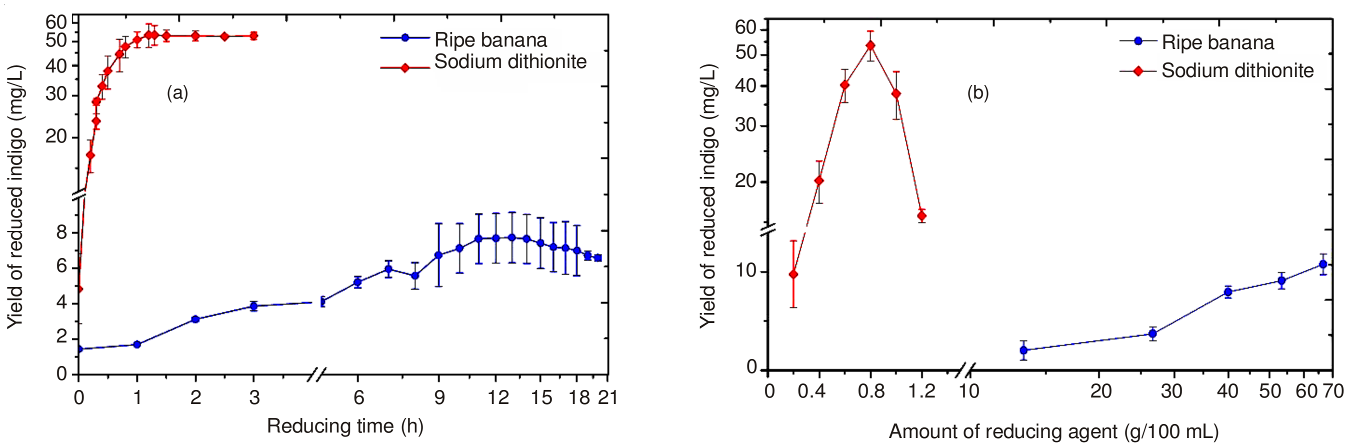

Fig. 1. Reduction of indigo dye by ripe banana and sodium dithionite (a) at various reducing times (b) at various amount of reducing agent

essentially being reached to equilibrium. However, ripe banana exhibited the shorter time required to reach equilibrium compared to sodium dithionite. Since the higher adsorption rate at the initial period offered the large number of vacant adsorption sites available on cotton fabric. Thus the increase of temperature tends to enhance on the dye adsorption rate at the initial stages. At the equilibrium times, the indigo dye adsorbed decrease with the increase in temperature which indicated an exothermic process of adsorption. The plot of t/q_t and time Fig. 3 suggests that the experimental data for the indigo dye adsorption on cotton fabric using sodium dithionite and ripe banana as reducing agents fit well with the pseudo second order kinetic model.

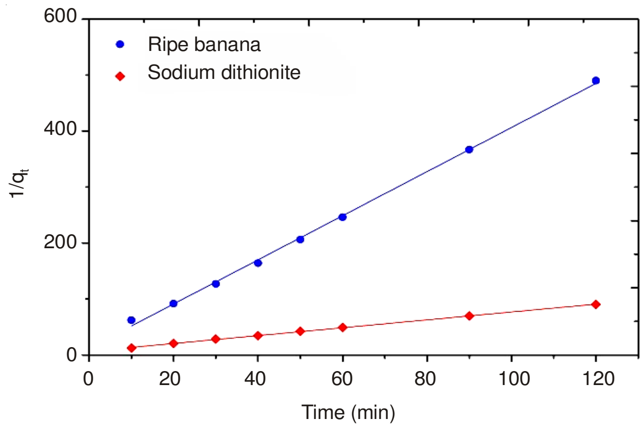

Fig. 3. Plot of the pseudo second equation at 30 °C for the adsorption of indigo dye on cotton fabric

The pseudo second-order rate constants k_2 at different temperatures were applied to estimate the activation energy (E_a) of the adsorption of indigo dye on cotton fabric through the Arrhenius equation, k = Aexp($-E_a$/RT), where k is the rate constant (g cotton/mg min) and E_a is the Arrhenius activation energy (kJ/mol). The plot of ln k and 1/T in Fig. 4 reveals that the activation energy of indigo dye adsorption on cotton fabric using ripe banana (26.18 kJ/mol) was higher than the energy required for indigo dyeing using sodium dithionite (16.96 kJ/mol). This may be due to the groups of leuco compound in the dye solution using banana as reduing agent are less attractive to cotton fabric than dye solution using sodium dithionite[8]. However, in both cases the indigo dye is not covalently bound to the fiber. From this it is inferred that the leuco-indigo molecules reach to the pour site of cotton during the dyeing and then is oxidized back to the indigo dye[8].

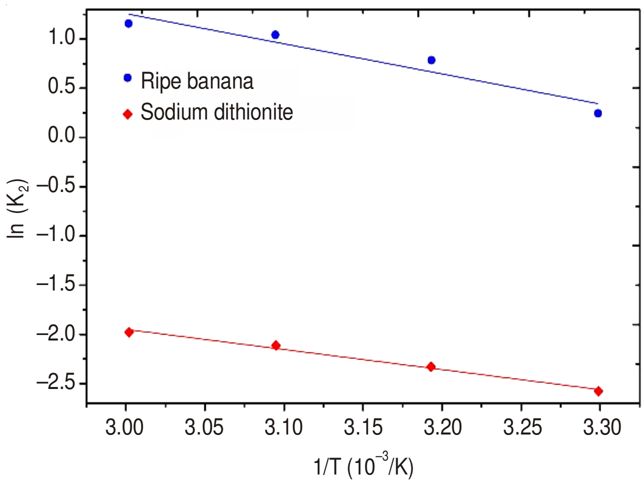

Fig. 4. Arrhenius plot for the indigo dye on cotton fabric using various reducing agent

Batch equilibrium study: The study of equilibrium isotherm model were examined in this study to describe the indigo dyeing on cotton fabric under the various initial dye concentration range are shown in Fig. 5. They were examined *via* the Langmuir model, $(C_e/q_e) = 1/Q_b + (1/Q)C_e$ where C_e (mg/L) is the concentration of indigo at equilibrium. b(mL/mg) is the Langmuir constant related to the affinity of binding sites and Q (mg/g cotton) is the adsorption capacity. The regression correlation coefficient of the Langmuir equation ($R^2 > 0.99$) in both reducing agents were observed in Fig. 6, that indicated a good fit of the equilibrium data. The monolayer adsorption capacity according to the Langmuir isotherm, was found to be 2.78 and 3.54 mg/g cotton at 30 °C for ripe banana and sodium dithionite as reducing agent, respectively.

Evaluation of thermodynamic data: The thermodynamic parameters; standard Gibbs free energy change (ΔG°) and the

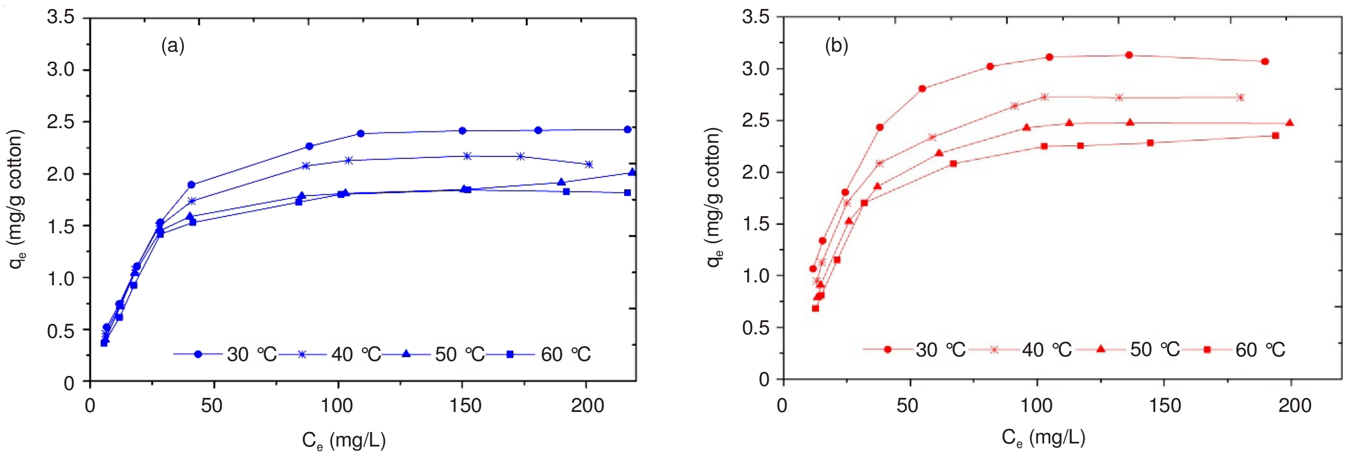

Fig. 5. Equilibrium adsorption of indigo dye on cotton fabric using (a) ripe banana and (b) sodium dithionite at various temperatures

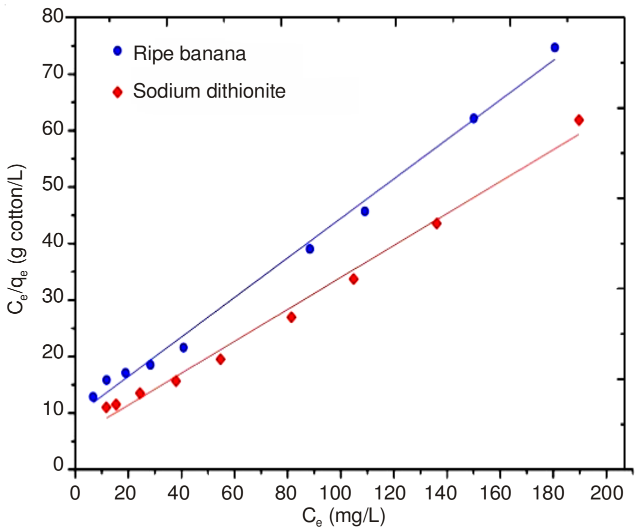

Fig. 6. Langmuir plot of the indigo dye on cotton fabric using various reducing agent at 30 °C

equilibrium constant (K_c) for indigo adsorption process can be evaluated using equations, $K_c = C_{ad,e}/C_e$ and $\Delta G° = RT \ln K_c$ where K_c is the equilibrium constant, $C_{ad,e}$ and C_e are the dye concentration adsorbed (mg/L) at equilibrium and the concentration of dye (mg/L) left in the dye bath at equilibrium, respectively, T is the solution temperature (K) and R is the gas constant (8.314 kJ/mol). On the other hand, using the experimental values of K_c obtained at different temperature, it would be possible to estimate the standard enthalpy change (ΔH°) and standard entropy change (ΔS°) from the slope and intercept of van't Hoff' plot between ln K_c *versus* 1/T are shown in Fig. 7[9-11].

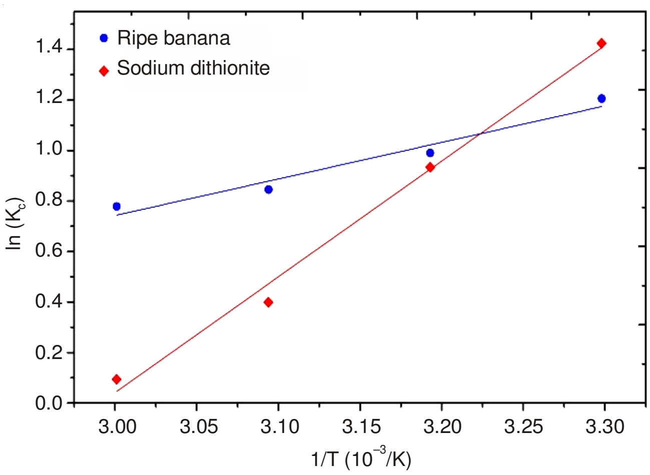

Fig. 7. van't Hoff plot of the adsorption of indigo dye on cotton fabric

From Table-1, the ΔG° in all the cases were negative, indicated that the adsorption of indigo dye on cotton fabric using both reducing agent are spontaneous. Furthermore, the adsorption process using sodium dithionite as reducing agent was a higher indigo adsorption evidently presented by the larger value of K_c. Moreover, the higher the temperature, the less indigo adsorption occurred for both reducing agents. Since the ΔH° and ΔS° were both negative, therefore, the indigo adsorption process using both reducing agents were exothermic and the adsorption of indigo dye become more restrained within the cotton than in the dyeing solution (as the leuco indigo).

TABLE-1
THERMODYNAMIC PARAMETERS FOR THE ADSORPTION OF INDIGO DYE ON COTTON FABRIC AT DIFFERENT TEMPERATURES

Temperature (°C)	K_c	ΔG°	ΔH°	ΔS°	R^2
Sodium dithionite					
30	4.16	-3.55	-38.08	-113.93	0.9923
40	2.54	-2.41			
50	1.49	-1.27			
60	1.10	-0.13			
Ripe banana					
30	1.20	-2.96	-12.03	-29.94	0.9601
40	0.99	-2.66			
50	0.85	-2.36			
60	0.78	-2.06			

Evaluation of colorimetric data: The colorimetric data offered the maximum absorption at 660 nm for the dyed cotton fabrics using sodium dithionite and ripe banana as reducing agents. The dyed cotton fabric using banana gave a lighter color strength (K/S) due to the increase in lightness (L^*) comparing to sodium dithionite (Table-2). Moreover, using ripe banana as reducing agent gave deeper color on cotton fabric color by repeatedly dyeing 8-10 times (data not shown).

TABLE-2
COLORIMETRIC DATA FOR SAMPLES

Reducing agent	K/S	L*	a*	b*
Ripe banana	0.50	83.41	-2.11	-7.11
Sodium dithionite	1.63	63.65	-2.17	-17.72

Conclusion

This work aims to investigate the efficiency of ripe banana to be used as a reducing agent in traditional indigo dyeing on cotton fabric as possible substitutes for the environmentally unfavourable sodium dithionite. The reduction of indigo dye could successfully be applied at the optimum condition of pH about 13 at 30 °C. The optimal conditions of the kinetic studies were a material to liquor ratio (MLR) of 1:100 and 60 min contact time. The overall rate of the indigo dye adsorption on cotton fabric was controlled by the pseudo second order reaction.The activation energy of the dye adsorption using ripe banana was higher than the energy required to dye on cotton fabric using sodium dithionite. The equilibrium adsorption data followed the Langmuir model. The thermodynamic parameters such as Gibbs free energy change, enthalpy change and entropy change terms were the negative values. They were shown that the indigo dye adsorption is a exothermic and spontaneous process. However, the cotton fabric dyeing using ripe banana as reducing agent gave a longer reducing time, a larger amount of reducing agent for reduction process and higher activation energy compared to using sodium dithionite. Further more, the dyed cotton fabric using ripe banana to reduce indigo dye gave a lighter color than using sodium dithionite.

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