

Adsorption Study of Acid Dyes for Nylon with the Adsorbent Derived from Tamarind-Seed Testa

P. Jutamaneerat, J. Setthayanond, P. Tootompong

Abstract: Adsorbent material derived from tamarind-seed testa was studied for acid dye adsorption. Acid dyes are water-soluble dyes preferred for industrial dyeing of nylon. In this research, the dye adsorbed efficiencies of three readily water-soluble acid dyes, namely Nylosan Red E-BL (NR), Nylosan Yellow S-L sgr (NY) and Moderacid Yellow GL (MY) were investigated. From the results, it was found that 1 kg tamarind seeds could be prepared into 55 g adsorbent material. The adsorbent was capable of adsorbing the acid dyes well under pH 5 condition with a rapid adsorption taking place within the first 15 minutes of adsorption process. After that, the adsorption increased gradually until reaching equilibrium after 2-3 hours depending on the structures of acid dyes. Adsorption behavior of NR was fitted with both Langmuir and Freundlich isotherms while NY and MY adsorptions corresponded to Langmuir and Freundlich isotherms, respectively.

Keywords - Acid dyes, tamarind-seed testa, adsorbent, wastewater treatment, nylon

I. INTRODUCTION

At present, color plays an important role in influencing human's feeling and life. Apart from user preference, selection of wearing colored clothes also very well reflects the feeling and emotion of users in their daily life. As a demand of wide variety of color in clothing, there are more than 100,000 dyestuffs accounted for 1 million tons annually, being used in the textile industry (Forgacs, Cserháti et al. 2004, Gupta and Suhas 2009). Such a large quantity of dyestuffs employed poses a serious effect to wastewater treatment process as the effluent released from dyeing process contained a larger amount of dyes. This is even more serious if the dyes are those from water soluble type, for example, acid and reactive dyes. These dyes cannot be removed by coagulation process. Besides, using biological breakdown process may cause a generation of carcinogenic entities from some dyestuff degradation (Melgoza, Cruz et al. 2004, Saratale, Saratale et al. 2011).

Tamarind is a tropical plant being well cultivated in hot and humid countries like Thailand. Tamarind fruits are widely consumed as a fresh fruit and also as a flavor ingredient for food cooking. The flesh of tamarind fruits is also processed into variety of food products and a large amount of tamarind seeds is by-products of this process. Tamarind seed kernel can be used to prepare a thickener and stabilizer. In the textile industry, tamarind seed kernel can be employed as a sizing agent (Gidley, Lillford et al. 1991, Nishinari, Takemasa et al. 2009) or thickener for fabric printing (Tepparin, Porntip et al. 2011). A water-soluble, natural colorant can also be prepared from tamarind seeds and it is well dyeable on silk and cotton fabrics with enhancing antibacterial properties to the fabrics (Tepparin, Sae-be et al. 2012). Tamarind-seed testa which is a water-insoluble, fibrous component with porosity can also well be used for adsorption of reactive dyes (Chaiyapongputti, Sae-Bae et al. 2014) and chromium contaminated in water (Setthayanond, Sae-Bae et al. 2017).

II. PROBLEM STATEMENT

Effluent released from chemical wet processing of textiles, especially dyeing process, strictly needs a proper treatment in order to meet water quality standard before release into natural water resources. However, frequent complaint has been raised from local communities nearby the dyeing factories due to visually noticeable color as a result of contaminated dye in the water. Even a small amount of dye can cause an obvious color contaminated in water. This brings a great concern to people living in nearby area that consume water from dye polluted resources. In addition, it also poses an adverse effect to water ecosystem. Another more important point is that if water is contaminated with water-soluble dyes like acid dyes, it will be difficult to remove such contaminants. Typical wastewater treatment processes e.g. coagulation, membrane filtration and biological process, cannot be used to remove this type of dye. The only process that works is adsorption. Nevertheless, dye adsorption process using activated carbon is costly. Alternatively, the way out for this is to develop the low-cost adsorbent from natural, agricultural residues.

The Aim of Research: In the current research, the adsorbent material was prepared from tamarind seed testa for adsorption of nylon acid dyes.

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* Correspondence Author (s)

P. Jutamaneerat, Department of Textile Science, Faculty of Agro-Industry, Kasetsart University Bangkok, Thailand.

J. Setthayanond, Department of Textile Science, Faculty of Agro-Industry, Kasetsart University Bangkok, Thailand.

P. Tootompong, Department of Textile Science, Faculty of Agro-Industry, Kasetsart University Bangkok, Thailand.

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As acid dyes are highly water soluble, it is difficult to remove from the dyehouse effluent. Adsorption using bio-adsorbent is a promising method for dye removal. This would take part in helping relief tension between local community and the textile factories and also give a positive response to the utilization of residual materials from industrial tamarind processing.

III. METHOD OF RESEARCH

Preparation of adsorbent material: Tamarind seeds, purchased from the local market in Thailand, were washed and dried. Tamarind-seed testa were isolated by heating with Samsung GE872D, 850-watt microwave for 3 minutes. The seed testa were then boiled in water followed by 1% NaOH solution in order to remove the coloring matter. After that, they were bleached in the solution containing 50 g/l H₂O₂ and 5 g/l Na₂SiO₃ at pH 10-11, 100°C for 1 hour (Chaiyapongputti, Sae-Bae et al. 2014, Setthayanond, Sae-Bae et al. 2017). The obtained seed testa was neutralized by boiling in water for another 30 minutes and oven-dried before grinding into a fine powder adsorbent. The powder was sieved to the particle size of ≤ 300 μm. Surface morphology of the adsorbent powder was monitored with JEOL JSM-6610LV Scanning Electron Microscopy (SEM).

Adsorption study: Adsorption was studied on three acid dyes for nylon viz. Nylosan Yellow S-L sgr (NY), Nylosan Red E-BL sgr.180 (NR) from Achroma, Co., Ltd and Moderacid Yellow GL (MY) from Modern dyestuff, Co., Thailand. Experimental factors studied were pH (3-5) and contact time (15-300 min). Dye adsorption was conducted in 30 ml of 50 mg/l dye solutions in 100 ml-sized container with 45-mm diameter and 58-mm height and 1g adsorbent material was used in this study. Amount of adsorbed dye (q_e) was calculated from equation 1.

$$q_e = \frac{V}{m} (C_0 - C_e) \tag{1}$$

Where V is solution volume (ml), m is adsorbent dose (g), C₀ and C_e are initial and the residual dye concentrations (mg/l), respectively (Kamranifar, Khodadadi et al. 2018).

Isotherm studies: Langmuir and Freundlich are adsorption isotherm models usually used to explain adsorption behavior of material. Linear equation of Langmuir isotherm is depicted in equation 2. In the equation, Q denotes Mono-layer adsorbed efficiency of adsorbent (mg/g), C is concentration of dye solution after 3-hour adsorption and K_L denotes Langmuir adsorption constant related to adsorption energy (Mahmoud, Nabil et al. 2016).

$$\frac{C}{Q} = \frac{1}{q} C + \frac{1}{K_L q} \tag{2}$$

Freundlich isotherm is the model for describing multi-layer adsorption phenomena where adsorption on adsorbent material can occur repeatedly without reaching saturation point (Nassar and Khatib 2016). Linear relationship of Freundlich isotherm is shown in equation 3.

$$\log Q = \frac{1}{n} \log C + \log K_F \tag{3}$$

where Q is multi-layer adsorption efficiency of adsorbent (mg/g), C is concentration of solution after 3-hour adsorption, n and K_F are Freundlich adsorption constants.

IV. RESULTS & DISCUSSION

Preparation of adsorbent material: After getting rid of coloring matters and other hot water-soluble and also alkali-soluble (NaOH 1%) components from 1 kg tamarind seeds, 300 g tamarind-seed testa was obtained and later after treating the seed testa with H₂O₂, it yielded 55 g adsorbent material. The adsorbent obtained was in a white powder form. SEM image illustrates fibrous structures of tamarind seed testa and the prepared adsorbent as seen in Figure 1.

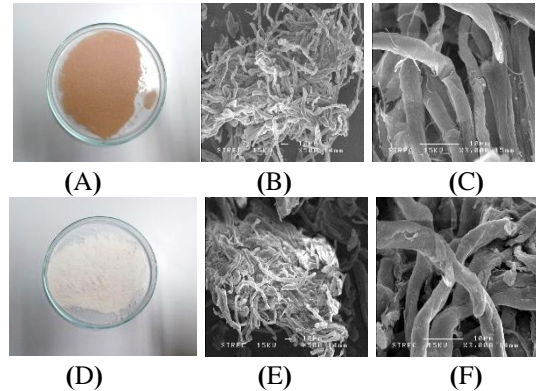


Figure 1. SEM images of tamarind-seed testa and adsorbent materials, (A) tamarind seed testa; (B) tamarind seed testa (500x); (C) tamarind seed testa (3,000x); (D) adsorbent (E) adsorbent (500x); (F) adsorbent (3,000x)

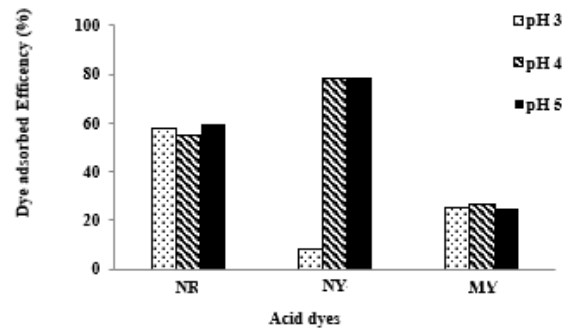


Figure 2. Acid dye adsorbed efficiency of adsorbent in pH 3-5 solutions at 24-hour contact time

Adsorption study: The results of acid dye adsorption on the adsorbent prepared from tamarind-seed testa in pH 3-5 dye solutions for 24 hours are shown in Figure 2. It was found that each acid dyes were adsorbed onto the adsorbent to different extents. Fortunately, this adsorbent exhibited an optimum dye adsorption at pH 4-5 that is similar to the pH condition used in acid dyeing for nylon. This facilitates application of this adsorbent in acid dyeing factories in which wastewater pH adjustment is not needed (Abdullah, Mukthy et al. 2016). The adsorbent adsorbed NY, NR and MY for 80%, 60% and 25%, respectively.



Table 1 shows the dye adsorbed efficiency of the adsorbent at different contact times and it was observed that the adsorption occurred rapidly within the first 15 minutes and the adsorbed efficiency gradually increased after that until reaching adsorption equilibrium. The adsorbent could adsorb NY, NR and MY dyed for approximately 75%, 50% and 25%, respectively.

Table 1. Adsorbed efficiencies of acid dyes for nylon in the pH 5 solution at different contact times

Contact time (min.)	Adsorbed efficiency (%)		
	NR	NY	MY
15	50.47	69.04	20.99
30	49.06	73.99	26.73
60	50.54	76.76	24.30
90	51.40	76.59	23.58
120	50.18	75.02	27.85
180	47.96	78.25	25.04
240	50.06	74.59	25.51
300	51.08	75.89	25.59

Adsorption rates of NR, NY and MY dyes in pH 5 solutions took place rapidly within the first 60 minutes. After that, the adsorption rate was slowed down until reaching adsorption equilibrium. From statistical analysis at 95% confidence interval ($\rho < 0.05$), NR and MY dyes reached equilibrium within 120 minutes whereas NY required longer time of 180 minutes. Therefore, adsorption isotherms of

these three acid dyes were investigated using 3-hour contact time.

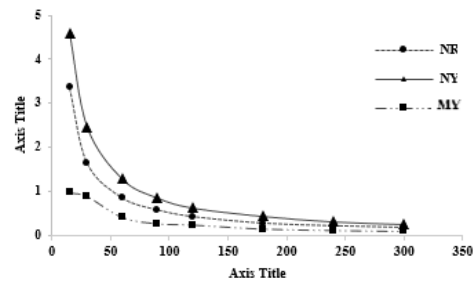


Figure 3. Adsorption rates of acid dyes in pH 5 solutions

Isotherm: Adsorption isotherms of the acid dyes on the adsorbent were studied according to Langmuir and Freundlich theories. Dye adsorption was conducted in pH 5 solution for 3 hours and the results can be seen in Figures 4-5 for Langmuir and Freundlich isotherms, respectively. The three acid dyes displayed different adsorption mechanism on the adsorbent material. NR exhibited a combined mono- and multi-layer adsorptions, indicating both physical and chemical binding to the adsorbent but for NY, mono-layer adsorption occurred rather than the multi-layer one. While MY tended to exhibit physical adsorption according to Freundlich isotherm. The adsorbent could better adsorbed NY than NR and MY.

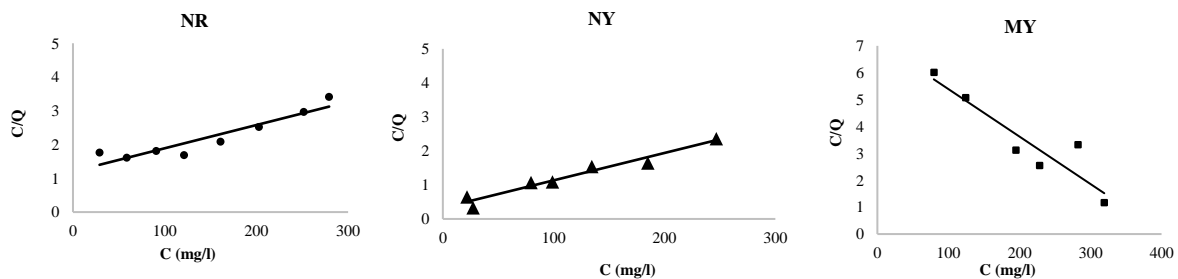


Figure 4 Langmuir adsorption isotherm

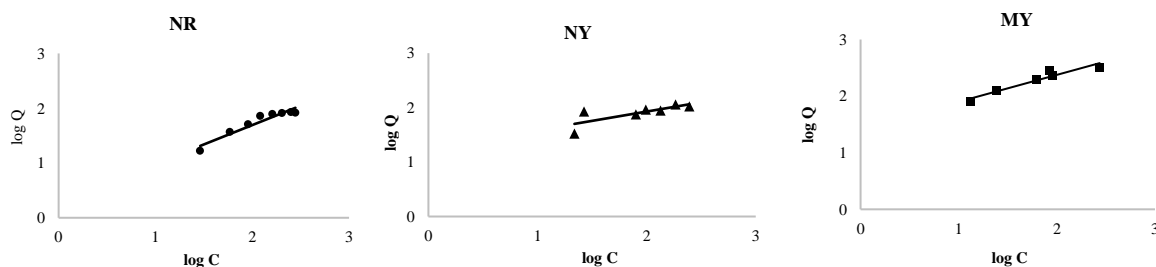


Figure 5 Freundlich adsorption isotherm

Table 2. Correlation constants of the adsorption models of acid dyes

Dye	Code	Langmuir			Freundlich		
		q	$K_L (x10^{-3})$	R^2	n	K_F	R^2
Nylosan Red E-BL	NR	144.9275	0.20	0.8735	1.4152	1.8985	0.9161
Nylosan Yellow S-L sg	NY	123.4568	1.42	0.9518	2.9283	17.5509	0.6035
Moderacid Yellow GL	MY	-	-	-	2.1022	26.5461	0.9182

V. CONCLUSION

The adsorbent prepared from tamarind seeds could adsorb acid dyes used for nylon dyeing and the optimum adsorption pH was observed in vicinity of 5. Such pH condition gave advantage to using this adsorbent for acid dye adsorption as acid dyeing was usually carried out in acidic condition. Thus, it facilitates adsorption process, in addition, no need of mechanical agitation required. The adsorbent could adsorb Nylosan Yellow S-L sgr, Nylosan Red E-BL and Moderacid Yellow GL for more than 75%, 60% and 25%, respectively. Each dyes exhibited different adsorption behavior on the adsorbent. NR and MY adsorption reached equilibrium after 2 hours while NY spent 3 hours to reach adsorption equilibrium. NR adsorption took place in both mono- and multi-layer manners, informing the occurrence of both physical and chemical adsorptions. In the case of NY, adsorption followed mono-layer chemical adsorption model, while MY displayed a multi-layer adsorption mechanism.

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