

Kinetic and Efficiency of Reactive Dye Sorption by Plant Biomass

Sunantha Laowansiri

Faculty of Environment and Resource Studies, Mahasarakham University, Muang,
44000 Mahasarakham, Thailand

Abstract: This research study shows the efficiency and kinetic of Reactive Red 141 (RR 141) adsorption using Cattail (CT), Water Lettuce (WL) and Activated Carbon (AC) sorbents. The sorbents were dried and sieved 100-200 mesh sizes (0.125-0.150 mm). Simulated textile wastewater 50 mL was prepared by RR 141 of 50 mg L⁻¹ and 1,300 mg COD L⁻¹. After that fill 1.0 g sorbents and then agitated at 130 rpm in a shaker at temperature of 25°C and adjust pH was 7±0.02 for 1440 min. Results revealed that the efficiency of RR 141 removal by CT, WL and AC were 64.84, 85.02 and 94.98%, respectively. The kinetics of RR 141 adsorption fitted for pseudo-second order. Results revealed that AC was higher and the removal of RR 141 was faster than WL and CT, respectively. However, AC gave a higher RR 141 sorption capacity than WL and CT, respectively. The q_e values of CT, WL and AC were 1.63, 3.56 and 8.52 mg g⁻¹, respectively.

Key words: Adsorption, kinetic, plant biomass, reactive dye, wastewater, temperature

INTRODUCTION

Textile industries consume large volumes of water and chemicals for the wet processing of textiles. The presence of very low concentrations of dyes in effluent discharged from these industries is highly visible and undesirable (Nigam *et al.*, 2000). Brightly colored, water soluble reactive dyes are the most problematic as they tend to pass through conventional treatment systems unaffected (Willmott *et al.*, 1998).

Due to their chemical structure, dyes are resistant to fading when exposed to light, water and many chemicals (Poots *et al.*, 1976; McKay, 1979). Dyes usually have a synthetic origin and complex aromatic molecular structures which make them more stable and more difficult to biodegrade. Various physical, chemical and biological methods have been used for the treatment of dye containing wastewater. Some chemical oxidation by Fenton reagent, ozone, UV plus H₂O₂ or NaOCl results in aromatic ring cleavage and may generate chemical sludge or by products that are likely to be more toxic (Robinson *et al.*, 2000). Aerobic biological treatment is known to be ineffective for dye removal but anaerobic bioremediation enables water-soluble dyes to be decolorized (Carliell *et al.*, 1996; Laowansiri *et al.*, 2008).

Physical adsorption technology, i.e., by activated carbons has gained favor recently because it has a high efficiency in the removal of highly stable dyes and is economically feasible when compared to other methods (Choy *et al.*, 1999). However, activated carbons are expensive and not easily regenerated (Robinson *et al.*, 2000). Although, ion exchange resins can be regenerated

easily, the high cost hinders their wide application for the treatment of dye bearing wastewater. Consequently, low cost sorbents able to bind dye molecules and easily regenerated have been extensively researched and tested (Robinson *et al.*, 2000; Won *et al.*, 2004). Many studies have been undertaken to find low-cost sorbents which include peat, bentonite, steel-plant slag, fly ash, China clay, maize cob, wood shavings and silica. However, these low-cost sorbents generally have low uptake which means that large amounts of sorbents are needed.

Although, good sorption capacities for reactive dyes (60-420 mg g⁻¹) are found for quaternized organic materials such as cellulose, sugarcane bagasse, rice husk and coconut husk, successful regeneration has not been reported (Karcher *et al.*, 2002).

Therefore, new, economical, easily available and highly effective sorbents still need to be found. In this study, the sorbents of Cattail (CT), Water Lettuce (WL) and Activated Carbon (AC) were used and evaluated as a possible sorbent for the treatment of an anionic reactive dye, Reactive Red 141 (RR 141).

In addition, the effectiveness of this biosorbent on the removal of reactive dye was compared with that of activated carbon for comparative evaluation.

MATERIALS AND METHODS

Simulated textile wastewater: Simulated textile wastewater consists of modified starch as carbon source (1300 mg COD L⁻¹) together with 50 mg L⁻¹ of Reactive Red 141 (Evercion Red H-E7B). RR 141 obtained from

Table 1: The composition of simulated textile wastewater

Composition	Concentration (mg L ⁻¹)
NaCl	150.00
(NH ₄) ₂ SO ₄	280.00
NH ₄ Cl	230.00
Na ₂ HPO ₄	380.00
Na ₃ HPO ₄ ·12H ₂ O	123.00
MgSO ₄ ·7H ₂ O	5.00
FeCl ₂ ·4H ₂ O	6.00
CoCl ₂ ·6H ₂ O	0.88
H ₃ BO ₃	0.10
ZnSO ₄ ·7H ₂ O	0.10
CuSO ₄ ·5H ₂ O	0.05
NiSO ₄ ·6H ₂ O	1.00
MnCl ₂ ·4H ₂ O	5.00
(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	0.64
CaCl ₂ ·2H ₂ O	5.00
NaHCO ₃	1500.00
Modified starch	1300.00
Reactive red 141	50.00

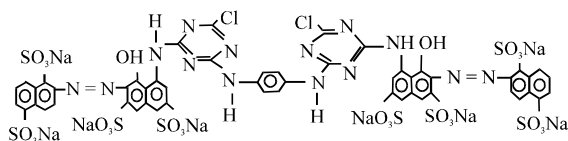


Fig. 1: Chemical structure of C.I. Reactive Red 141

Winimex Co., Ltd. (Thailand) was used in this study. The chemical structure is shown in Fig. 1. The composition of a simulated textile wastewater is shown in Table 1 (Prakash and Gupta, 2000). The pH was adjusted to 7.00 ± 0.02 using 0.1 N NaOH and 0.1 N H₂SO₄.

Sorbents preparation: About 3 sorbents were Cattail (*Typha* sp., CT), Water Lettuce (WL) and Activated Carbon (AC). The CT and WL were collected from natural pond, Mahasarakham province, Thailand. Having washed the leaves of the CT and WL with distilled water, it dried in the sun for 2-3 weeks on a small ground. CT and WL were prepared by sieving to 100×120 meshes (0.125-0.150 mm) to produce a uniform size range. After being sieved, the CT and WL were dried at 105°C for 24 h and stored in the desiccators until use.

Untreated charcoal-based Activated Carbon (AC) was used in this study. AC was prepared by sieving to 100×120 meshes (0.125-0.150 mm) to produce a uniform size range. After being sieved, the AC was washed with distilled water and then it was dried at 105°C for 24 h and stored in the desiccators until use.

Sorbent characterization: The dried CT, WL and AC were ground to the particle size range of 0.125-0.150 mm. The functional groups located on algal surface were specified using Fourier Transform Infrared Spectrophotometer (FTIR), Perkin Elmer, Model 1760X.

Sorption experiments: Sorption experiments were carried out in a batch process by using simulated textile wastewater. The sorption kinetics were carried out by agitating 50 mL of simulated textile wastewater solution of 50 mg L⁻¹ of initial RR 141 concentration with 1.0 g of sorbents in a vessel maintained at 25°C. The pH during the experiments was controlled at 7 ± 0.02 . The mixture was gently shaken at 130 rpm on a rotary shaker for 1440 min. After shaking the vessel for predetermined time intervals, the samples were taken and centrifuged for liquid-solid separation and measured. The samples were collected to analyze for the residue dye under a certain time interval using spectrophotometer.

Analytical procedure: The Chemical Oxygen Demand (COD: closed reflux titrimetric method) and Suspended Solids (SS) were measured according to the procedure outlined in Standard Methods (APHA, 1998). Color measurements in clarified samples were centrifuged at 6,000 rpm for 10 min and the absorbance values of supernatants were determined. Absorbance of reactive red 141 solution was measured at maximum wavelengths of 546 nm using an UV-Visible recording spectrophotometer (Uvi Light-SECOMAM, France). pH was measured using a digital pH meter type C532 (Belgium). The functional groups located on sorbents surface were specified using Fourier Transform Infrared Spectrophotometer (FTIR), Perkin Elmer, Model 1760X.

RESULTS AND DISCUSSION

Sorbent characterizations: The possible functional groups on CT, WL and AC surface were shown in Table 2 which showed that the functional groups of CT were C, C = C (nonconjugated, noncyclic), C = C (cyclic or conjugated), Alkyl, Hydroxyl, Carbonyl, Phenyl, C = N, NH, (CH₃)₃C-, Si-O-Si and Si-O-C. The functional groups of WL were C, C = C (nonconjugated, noncyclic), C = C (cyclic or conjugated), Alkyl, Amine C = N, NH, Ph-CH₃, Si-O-Si and Si-O-C and meanwhile, the functional groups of AC were C, C = C (nonconjugated, noncyclic) and C = C (cyclic or conjugated).

Reactive dye removal: Simulated textile wastewater 50 mL was prepared by RR 141 of 50 mg L⁻¹ and 1,300 mg COD L⁻¹. After that fill 1.0 g sorbents and then agitated at 130 rpm in a shaker at temperature of 25°C and adjust pH to 7 ± 0.02 for 1440 min. Found that the efficiency of color removal from RR 141 occurred rapidly in the initial time and increased with increasing duration time. Figure 2 and 3 shows the efficiency of RR 141 removal at 50 mg L⁻¹ initial concentration by using by CT, WL and

Table 2: Functional groups in dried of CT, WL and AC

Functional groups	CT	WL	AC
C	d	d	d
C = C (nonconjugated, noncyclic)	d	d	d
C = C (cyclic or conjugated)	d	d	d
Si-O-Si	d	d	n
Si-O-C	d	d	n
C = N	d	d	n
Alkyl; C-H	d	d	n
NH	d	d	n
Hydroxyl; O-H	d	n	n
Carbonyl; C = O	d	n	n
Phenyl; C ₆ H ₅ -	d	n	n
(CH ₂) ₂ C-	d	n	n
Ph-CH ₃	n	d	n
Amine; NH ₂	n	d	n

n = no-detected d = detected

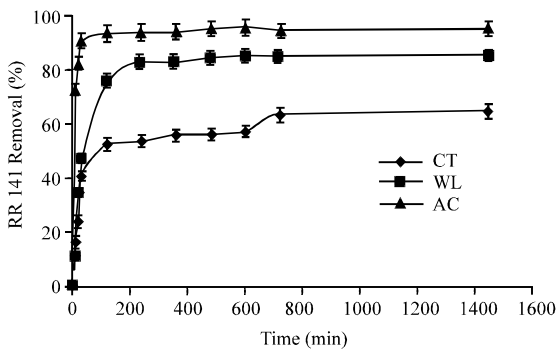


Fig. 2: RR 141 removal at 50 mg L⁻¹ initial concentration by using by CT, WL and AC sorbents

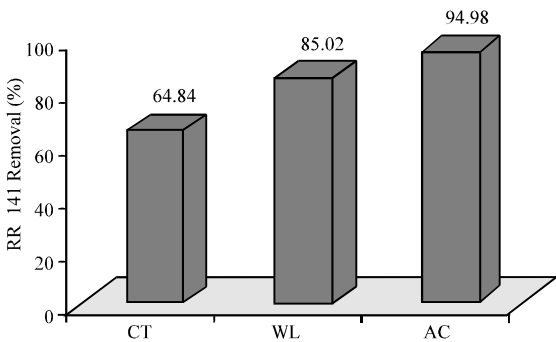


Fig. 3: Percentage of RR 141 removals at 50 mg L⁻¹ initial concentration by using CT, WL and AC at equilibrium time

AC sorbents. The results revealed that AC removed color more than WL and CT. As shown in Fig. 2 CT 64.84, WL 85.02 and AC 94.98%. Because AC is more porous, resulting dye adsorption RR141 well and as soon as possible.

The sorption of RR 141 removal by CT, WL and AC were investigated. The equilibrium times were 120 min for the CT, 240 min for WL and 30 min for AC. This finding suggested that the functional groups on CT, WL and AC

surfaces could have affinity with RR 141. The rates of sorption for each sorption system were also examined by applying the results with kinetic models.

Sorption kinetics: About 3 kinetic models, pseudo-first order, pseudo-second order and intra-particle diffusion models were employed to determine the kinetic nature of each sorption system. Pseudo-first order kinetic model has been widely used to predict the dye sorption kinetics. This can be expressed in a mathematical form as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (1)$$

The integrated form of Eq. 1 with initial/final conditions of: $q_t = 0$ at $t = 0$ and $q_t = q_e$ at $t = t$ is:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (2)$$

Where:

q_e = The amount of dye uptaken at equilibrium time (mg g⁻¹)

q_t = The amount of dye uptaken at time t (mg g⁻¹)

t = Time (min)

k_1 = The rate constant for the pseudo-first order model (min⁻¹)

The pseudo-first order rate constant, k_1 can be calculated from the plot of $\log(q_e - q_t)$ versus time t. The resulting k_1 value and R² for each sorption system are shown in Table 3.

A relatively low correlation coefficient implied that this first order model was not appropriate in describing such relationships. The pseudo-second order kinetic model derived by Ho and McKay (1999) on the other hand has been proven to be suitable for several sorption systems (Ho and McKay, 1998a, b; Fu and Viraraghavan, 2000; Banat *et al.*, 2003). This takes the following mathematical form:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (3)$$

Integrating Eq. 3 with initial/final conditions of: $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_e$ gives:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

where, k_2 is the pseudo-second order rate constant (g/mg/min). The linear plots of t/q_t versus t for the

Table 3: Comparison of kinetic parameter for the sorption of RR 141 at 50 mg L⁻¹ initial concentration by using CT, WL and AC sorbents

Sorption system	Pseudo-first order			Pseudo-second order		
	q _e (mg g ⁻¹)	k ₁ (min ⁻¹)	R ²	q _e (mg g ⁻¹)	k ₂ (g/mg/min)	R ²
CT	1.11	3.68×10 ⁻³	0.7353	1.63	1.61×10 ⁻²	0.9958
WL	1.32	9.67×10 ⁻³	0.9284	3.56	4.09×10 ⁻³	0.9944
AC	2.63	9.90×10 ⁻³	0.7560	8.52	1.56×10 ⁻³	0.9934

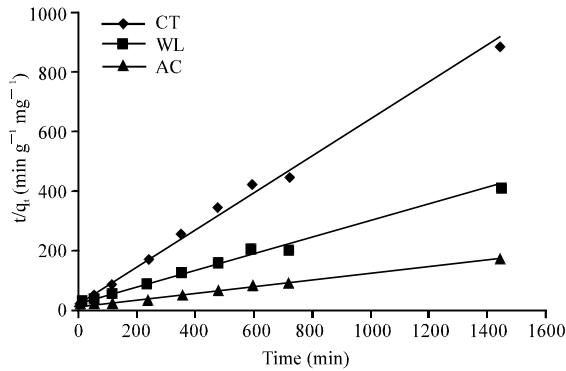


Fig. 4: Pseudo-second order kinetic of RR 141 at 50 mg L⁻¹ initial concentration by using CT, WL and AC sorbents

pseudo-second order in Eq. 4 were obtained for all sorption systems as shown in Fig. 4. q_e and k₂ can be directly determined from the slope and intercept of the plot. The model parameters are also shown in Table 3. The q_e values calculated from the pseudo-second order are in good agreement with the experimental data, q_{e, exp} and the extremely high R² (>0.993) for all sorption systems indicated that the sorption kinetics could be best described by this model.

This finding supported the assumption of the pseudo-second order model that the sorption process was due to chemisorption (Ho, 2003). In this case, chemical sorption could have occurred by the interaction between polar functional groups on the sorbent surface and dyes. Similar phenomena have been observed in the biosorption of Remazol Black B on biomass (Aksu and Tezer, 2000) and the sorption of Congo Red on activated carbon (Namarsivayan and Kavitha, 2007).

In order to understand the sorption mechanism, the functional groups on the algal surface were specified using FTIR technique. Table 2 shows the possible functional groups on the WL surface including amine and alkyl groups. The functional groups on the CT surface, including hydroxyl, carbonyl and alkyl groups. These functional groups can act as chemical binding agents. Carboxyl and hydroxyl groups can dissociate and become negative charge. That means these functional groups could attract the positive charge functional groups on dye structures and this is called Negative sorption which is

the sorption of the positive species by negative sorption sites (Volesky, 1990). On the other hand, the anionic reactive dye (RR 141) was negative charge with RR 141 not attached to functional groups of CT and WL. The surface of CT had more negative charge than WL, resulting less sorption. The pseudo-second order rate constants (k₂) for the sorption of RR 141 onto CT, WL and AC took the value of 1.61×10⁻², 4.09×10⁻³ and 1.56×10⁻³ g/mg/min, respectively. High k₂ suggested that the reactive dyes could be rapidly uptaken by the CT, WL and AC functional groups, respectively resulting in the system quickly reaching equilibrium as reported earlier. Hence, the k₂ results indicated that CT and WL could more rapidly sequester RR 141 when compared with AC.

However, AC gave a higher RR 141 sorption capacity than WL and CT, respectively. The q_e values of RR 141 by CT, WL and AC were 1.63, 3.56 and 8.52 mg g⁻¹, respectively. Marungrueng and Pavasant (2007) described the sorptions (sorption) of three basic dyes, Astrazon Blue FGRL (AB), Astrazon Red GTLN (AR) and Methylene Blue (MB) onto green macroalga *Caulerpa lentillifera* were investigated. The results were compared to the sorption performance of a commercial activated carbon (CARBON). The results revealed that the alga exhibited greater sorption capacities than activated carbon for the 3 basic dyes. The sorption process for all mixture systems (ALGA/AB, ALGA/AR, ALGA/MB, CARBON/AB, CARBON/AR and CARBON/MB) obeyed the pseudo-second order kinetic model. *C. lentifera* could more rapidly sequester AR when compared with activated carbon but was slower in the sorption of AB. For the sorption of MB, both ALGA and CARBON seemed to have the same sorption rate.

CONCLUSION

The efficiency of RR 141 removal by CT, WL and AC were 64.84, 85.02 and 94.98%, respectively. The kinetics of RR 141 adsorption fitted for pseudo-second order. Results revealed that AC was higher and faster than WL and CT in RR141 removal. The kinetics of RR 141 sorption fitted for pseudo-second order. The AC sorbent had higher RR 141 sorption capacity than WL and CT, respectively. The q_e values of CT, WL and AC were 1.63, 3.56 and 8.52 mg g⁻¹, respectively with the previous records.

NOMENCLATURE

- k_1 = Sorption rate constants for pseudo-first order kinetic equation (min^{-1})
 k_2 = Sorption rate constants for pseudo-second order kinetic equation (g/mg/min)
 $q_{e, \text{exp}}$ = Equilibrium dye concentration per unit mass of sorbent obtained from experiments (mg g^{-1})
 q_t = Amount of dye sorbed per unit mass of sorbent at time t (mg g^{-1})
 R^2 = Linear regression coefficient
 t = Time (min)

ACKNOWLEDGEMENTS

The researcher acknowledges Mahasarakham University and National Research Council of Thailand (NRCT) for their facilities and financially supporting this research.

REFERENCES

- APHA, 1998. Standards Methods for Examination of Water and Wastewater. 20th Edn., American Public Health Association, Washington, DC.
- Aksu, Z. and S. Tezer, 2000. Equilibrium and kinetic modelling of biosorption of Remazol Black B by *Rhizopus arrhizus* in a batch system: Effect of temperature. *Process Biochem.*, 35: 431-439.
- Banat, F., S. Al-Asheh and L. Al-Makhadmeh, 2003. Evaluation of the use of raw and activated date pits as potential adsorbents for dye containing waters. *Process Biochem.*, 39: 193-202.
- Carliell, C.M., S.J. Barclay and C.A. Buckley, 1996. Treatment of exhausted reactive dye bath effluent using anaerobic digestion: Laboratory and full scale trials. *Water SA.*, 22: 225-233.
- Choy, K.K.H., G. McKay and J.F. Porter, 1999. Sorption of acid dyes from effluents using activated carbon. *Resour. Conserv. Recycl.*, 27: 57-71.
- Fu, Y. and T. Viraraghavan, 2000. Removal of a dye from an aqueous solution by fungus *Aspergillus niger*. *Water Qual. Res. J. Can.*, 35: 95-111.
- Ho, Y.S. and G. McKay, 1998a. Kinetic model for the sorption of dye from aqueous solution by wood. *Process Safety Environ. Prot.*, 76: 183-191.
- Ho, Y.S. and G. McKay, 1998b. The kinetics of sorption of basic dyes from aqueous solution by *Sphagnum moss* peat. *Can. J. Chem. Eng.*, 76: 822-827.
- Ho, Y.S. and G. McKay, 1999. Pseudo-second order model for sorption processes. *Process Biochem.*, 34: 451-465.
- Ho, Y.S., 2003. Removal of copper ions from aqueous solution by tree fern. *Water Res.*, 37: 2323-2330.
- Karcher, S. and A. Kornmuller and M. Jekel, 2002. Anion exchange resins for removal of reactive dyes from textile wastewaters. *Water Res.*, 36: 4717-4724.
- Laowansiri, S., S. Vinitmantharat, P. Chaiprasert and S.R. Ha, 2008. Anaerobic degradation kinetics of reactive dye with different carbon sources. *J. Environ. Biol.*, 29: 309-314.
- Marungrueng, K. and P. Pavasant, 2007. High performance biosorbent (*Caulerpa lentillifera*) for basic dye removal. *Bioresour. Technol.*, 98: 1567-1572.
- McKay, G., 1979. Waste color removal from textile effluents. *Am. Dyes Rep.*, 68: 29-36.
- Namarsivayan, C. and D. Kavitha, 2007. Removal of congo red from water by adsorption onto activated carbon prepared from coir pith. *Dye Pigments*, 54: 47-58.
- Nigam, P., G. Armour, I.M. Banat, D. Singh, R Marchant, A.P. McHale and G. McMullan, 2000. Physical removal of textile dyes from effluents and solid-state fermentation by dye-adsorbed agricultural residues. *Bioresour. Technol.*, 72: 219-226.
- Poots, V.J., G. Mckay and J.J. Healy, 1976. The removal of acid dye from effluent using natural adsorbents-II wood. *Water Res.*, 10: 1061-1066.
- Prakash, S.M. and S.K. Gupta, 2000. Biodegradation of tetrachloroethylene in upflow anaerobic sludge blanket reactor. *Bioresour. Technol.*, 72: 47-54.
- Robinson, T., G. Mc Mullan, R. Marchant and P. Nigam, 2000. Remediation of dyes in textile effluents: A typical review on current treatment technologies with a proposed alternative. *Bioresour. Technol.*, 77: 247-255.
- Volesky, B., 1990. Biosorption of Heavy Metals. CRC Press, Boca Raton, USA.
- Willmott, N., J. Guthrie and G. Nelson, 1998. The biotechnology approach to colour removal from textile effluent. *J. Soc. Dyres Colourists*, 114: 38-41.
- Won, S.W., S.B. Choi, B.W. Chung, D. Park, J.M. Park and Y.S. Yun, 2004. Biosorptive decolorization of Reactive Orange 16 using the waste biomass of *Corynebacterium glutamicum*. *Ind. Eng. Chem. Res.*, 43: 7865-7869.