World Applied Sciences Journal 15 (3): 415-421, 2011
ISSN 1818-4952

Utilization of Modified *Gloriosa superba* Waste as an Adsorbent for the Removal of Reactive Dyes from Aqueous Solutions

[1]S. Ramalakshmi, [2]R. Selvakumar, [1]K. Muthuchelian and [3]K. Swaminathan

[1]Department of Bio-Energy, School of Energy,
Environment and Natural Resources, Madurai Kamaraj University, Madurai-625021
[2]Nanobiotechnology, PSG Institute of Advanced Studies, Coimbatore-641 004
[3]Department of Microbial Biotechnology, Bharathiar University,
Coimbatore 641016, Tamilnadu, India

Abstract: Carbon prepared from *Gloriosa superba* pericarp was used to remove reactive orange 107 and reactive black 5 from aqueous solution by adsorption technique under varying conditions of agitation time, dye concentration, adsorbent dose and pH. Adsorption depended on solution pH, dye concentration, carbon concentration and contact time. Equilibrium was attained at 165 minutes and 105 minutes for reactive orange 107 (RO 107) and reactive black (RB 5) dye, respectively. Increase in biomass dosage increased the adsorption. Adsorption capacity (Q_o) of Reactive black 5 was 23.92mg/g which was higher than Reactive orange 107 (21.72mg/g). The second-order kinetic model by Ho and Mckay described well the experimental data. Acidic pH was favorable for the adsorption of both dyes studied. Studies on pH effect and desorption show that chemisorptions seems to play a major role in the adsorption process. Among the reactive dyes studied, reactive black showed better adsorption capacity. Thus utilization of *Gloriosa superba* pericarp waste for reactive dye removal has potential application in dyeing industry wastewater treatment.

Key words: Gloriosa Superba Pericarp · Activated Carbon · Reactive Orange 107 · Reactive Black 5

INTRODUCTION

Reactive dyes are widely used in many industrial uses due to their bright color, excellent colorfastness and ease of application [1]. Reactive dyes are typically azo-based chromophores combined with different reactive groups, are highly recalcitrant to conventional wastewater treatment processes [2]. The adsorption method has been considered for the removal of textile dye effluents from wastewater and this method is superior compared with other traditional treatment methods due to its low cost, easy availability, simplicity of design, high efficiency, ease of operation and ability to treat a wide variety of dyes. The most commonly used adsorbent for the removal of dyes is commercial coal based activated carbon due to its high adsorption capacity and high surface area. However, its use is limited because of its high operation and regeneration costs. Thus there is continuing search for raw materials for carbonization to remove dyes are still going on. Researchers are trying to utilize locally available abundant resource that is mainly disposed as waste for this purpose to minimize the treatment cost. Even agricultural wastes such as coir pith [3] have been used for the removal of CBB dyes, also Calotropis gigantea [4] carbon have been used for methylene blue dye removal.

Gloriosa superba which is available in plenty in Africa, southeastern Asia and parts of Malaysia is a medicinal herb used in traditional medicine. Seeds of plant contain colchicines alkaloid, which is used in treatment of Gout disease, also in inducing capillary blood circulation. The seeds are exported to foreign countries for drug preparation, after which pericarp is usually dumped, add up to existing pollution problems.

The objective of the present study was to evaluate the feasibility of *Gloriosa superba* pericarp waste as a precursor for activated carbon production and employing the activated carbon thus prepared for the removal of reactive dyes from aqueous solutions.

Corresponding Author: S. Ramalakshmi, Department of Bioenergy, School of Energy, Environment and Natural Resources, Madurai Kamaraj University, Madurai-625021, India.

MATERIALS AND METHODS

Preparation and Characterization of Adsorbent: The pericarp was collected in and around agricultural fields of Coimbatore city, Tamilnadu, India. The samples were cut into small pieces, dried in sunlight until the moisture was partially evaporated and further dried in a hot air oven at 60°C for 24hr.the dried material was ground and sieved. The particle size of 125-250µm was used for reactive yellow and reactive black dye removal studies. Physical properties of carbon prepared from pericarp of *Gloriosa superba* (PGS) were analyzed. All the chemicals were of analytical reagent grade procured from Sigma, USA and Merck, India. All the solutions were prepared in double distilled water.

Adsorbate: Reactive orange 107, reactive black 5 dyes were procured from dye industry in Mumbai. The dye structure is given in figure 1. Reactive orange 107, reactive black 5 dyes are based on vinyl sulphone reactive group, which have negative charges in aqueous solutions. Standard solutions containing 10 to 50 mg/L of the dye were prepared by diluting a stock solution of 1000mg/L of Reactive orange 107, reactive black 5 dye studied. The analysis of RO 107, RB 5 was spectrophotometrically estimated by monitoring the absorbance at 415nm and 598nm using UV-VIS spectrophotometer (Shimazdu, UV-1601, Japan).

Batch Studies: Adsorption experiments were carried out by agitating 100mg of carbon with 50 mL of various adsorbate solution of concentration ranging from 10 to 50 mL and pH 7, 150 rpm and 30±2°C in a thermostated rotary shaker. The flasks were withdrawn at predetermined time intervals. The adsorbate and adsorbent were separated by centrifugation at 3000rpm for 20 min. The remaining adsorbate concentration in the supernatant was determined from which the amount of dye adsorbed by the adsorbent (q, mg/g) was calculated. Control experiments were carried without adsorbent to estimate the adsorbate removal due to adsorption onto the walls of the flasks. It was observed that adsorption onto the container walls were negligible. A study was carried out with different dosages of adsorbent 2(0.2-1.2g/50mL) for the equilibrium time to determine the effect of adsorbent dose on Reactive orange 107, reactive black 5 removal. The effect of pH on the adsorption process was studied by varying the pH of 50mL of 50mg/L adsorbate solution in the range of 2 to 9 using dilute HCl and NaOH solutions, while keeping the other experimental parameters at the values described earlier.

Desorption Studies: Desorption studies were carried out with adsorbate-laden adsorbent obtained from a batch process, in which the adsorbate solutions (30mg/L of Reactive orange 107, reactive black 5) were treated for the optimium contact time. The dye-laden carbon was washed gently with distilled water to remove unadsorbed dye. Several such samples were prepared. The spent adsorbent was then agitated at 200rpm for optimum contact time with 50 mL of distilled water and adjusted to different pH values in the range of 2 to 10. The desorbed dye was estimated spectrophotometrically as mentioned earlier. Similarly desorption studies were carried out separately in 50 mL of 0.1-0.5N NaOH solutions.

All experiments were carried out in duplicate and the mean values are presented. The error obtained was ±2%.

RESULTS AND DISCUSSION

Adsorbent Characterization: Characteristics of carbon prepared from pericarp of *Gloriosa superba* pericarp are presented in table 1. The decolorizing power was 75.9 mg/g, which indicated that the carbon prepared by the activation method had good adsorption capacity and it could be used for adsorption of organic dyes.

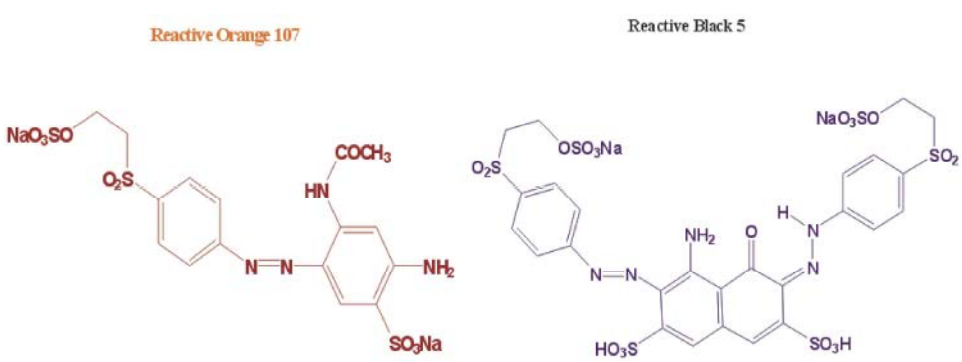


Fig. 1: Structure of Reactive Orange 107 and Reactive Black 5 Dye studied

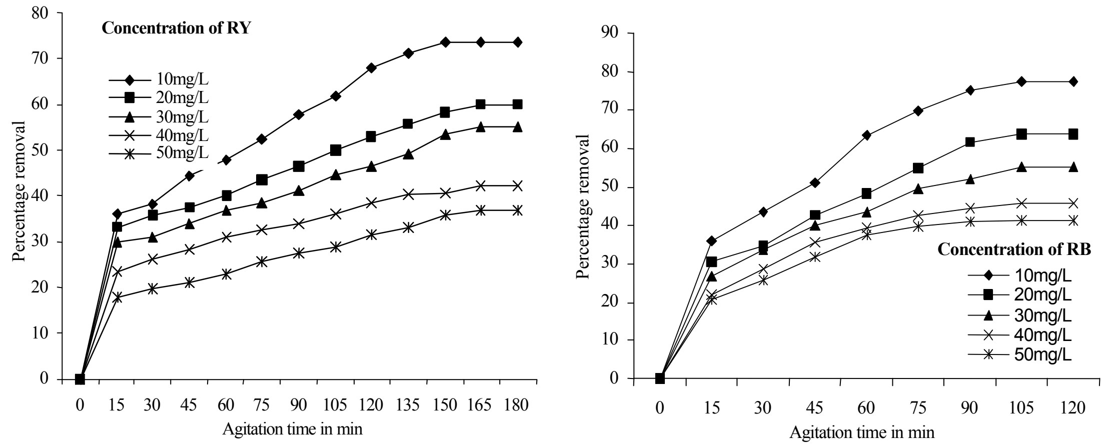


Fig. 2: Effect of Agitation time and initial dye concentration for (a) Reactive orange 107, (b) reactive black 5 adsorption onto carbon.

Table 1: Characteristics of carbon

Parameters	Value
pH	7.19
Moisture content	9.4
Ash content	0.282
Decolorising power (mg/g)	75.9
Porosity (%)	84.2
Ion exchange capacity (millieqiv/g)	0.2
Apparent density (g/ml)	0.255
Specific gravity	1.618
Water soluble matter (%)	3.75
Acid soluble matter (%)	19.9
Sodium (μg/g)	39.6
Potassium (μg/g)	274

Effect of Agitation Time and Initial Concentration on Dye Adsorption: The removal increases with time and attains equllibrium at 165 and 105 minutes for Reactive orange 107, reactive black 5 dyes, respectively for all the dye concentrations studied (Figure 2-a and -b). The curves were single, smooth and continuous till the saturation of dye on the carbon surface. Similar results were reported for various dye adsorption by other adsorbents [5, 6]. Equllibrium time is the one of important considerations in the design of water and wastewater treatment systems because it influences the size of reactor, thereby the plant economics [7]. The initial rapid phase may be due to availability of more number of adsorption/vacant sites, as a result there exists an increased concentration gradient between adsorbate in solution and adsorbate in the adsorbent [8].

The good adsorption capacity may be attributed to the micropores and mesopores structures present in the prepared carbon [9, 10].

Adsorption Kinetics: To study the adsorption kinetics, two kinetic models were used, which included Lagergren [11] and pseudo-second order models. In order to obtain the rate constants and equllibrium dye uptake, the straight-line plots of log were made at different initial dye concentrations.

If the intercept did not equal to the experimental equilibrium dye uptake then the reaction was not likely to be first order even if plot had high correlation coefficient with the experimental data [12]. The rate constants, predicted equilibrium uptakes and the corresponding correlation coefficients for all concentration tested are summarized in table 2.

For lagergren plot, correlation coefficients were from 0.7696 to 0.9731, but the calculated Q_e was not equal to experimental Q_e, suggesting the insufficiency of the model to fit the kinetic data for the initial concentrations examined. The reasons for these differences in the Q_e values was that there was a time lag, possibly due to a boundary layer/ external resistance controlling at the beginning of the adsorption process [13]. In most cases, the lagergren model does not fit the kinetic data well for the whole range of contact time and generally underestimate the Q_e values [12, 14].

The pseudo-second order model is based on the sorption capacity on the solid phase. Contrary to other well-established models, it predicts the behavior over the whole range of studies and it is in agreement with the chemisorptions mechanism being the rate controlling step [13]. This was consistent with the better results obtained with the pseudo-second order model (Tables 2, 3). Correlation coefficients were always higher than 0.99 and the lowest correlation coefficients in this case was

Table 2: Kinetic parameters for the reactive orange 107 dye adsorption at different initial dye concentrations.

Initial dye concentration (mg/L)	$(Q_e)_{exp}$ (mg/g)	Lagergren model K_1(L/min)	Q_e(mg/g)	R^2	Pseudo-second-order model K_2(g/mg min)	Q_e(mg/g)	R^2
10	7.35	0.021	7.3	0.8746	2.5	9.11	0.9724
20	12.0	0.018	10.1	0.8650	2.0	14.00	0.9726
30	16.47	0.018	14.4	0.7696	1.4	19.26	0.9646
40	16.92	0.018	12.5	0.9356	1.8	19.26	0.9863
50	18.35	0.019	18.1	0.8195	1.9	22.32	0.9618

Table 3: Kinetic parameters for the reactive black 5 dye adsorption at different initial dye concentrations.

Initial dye concentration (mg/L)	$(Q_e)_{exp}$ (mg/g)	Lagergren model K_1(L/min)	Q_e(mg/g)	R^2	Pseudo-second-order model K_2(g/mg min)	Q_e(mg/g)	R^2
10	7.72	0.038	10.2	0.9098	2.7	10.20	0.9806
20	12.72	0.034	15.8	0.8499	1.6	16.95	0.9714
30	16.56	0.028	15.0	0.9670	1.6	20.66	0.9912
40	18.20	0.040	21.0	0.9731	1.7	22.37	0.9967
50	20.60	0.052`	34.4	0.9441	1.6	25.38	0.9916

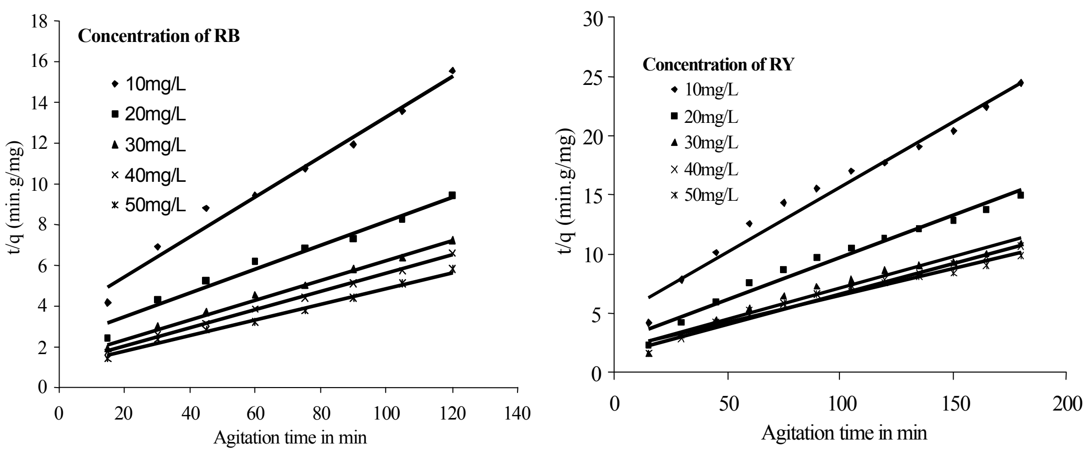


Fig. 3: Pseudo second order plots for (a) Reactive orange 107, (b) Reactive black 5 adsorption onto carbon

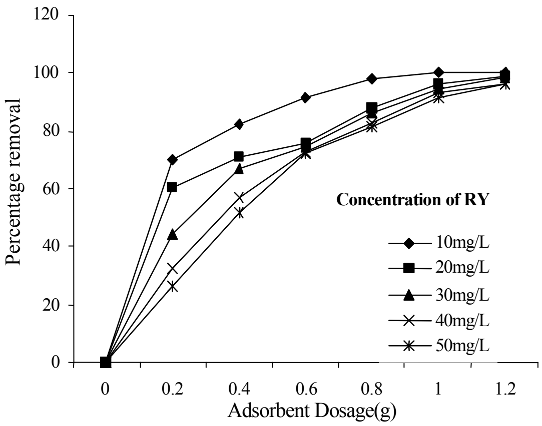
better than the first order model correlation coefficients (Fig 3a and b). The values of predicted equilibrium sorption capacities showed reasonably good agreement with the experimental equilibrium uptake value.

Effect of Carbon Dosage on RO 107 and RB 5 Removal: The removal of dye increased with increasing carbon dosage (0.2 to 1.2 g of carbon) respectively (Figure 4a and b). Increase in adsorbent dosage increased the percentage removal of dye which is due to the increase in adsorbent surface area consequent to the number of carbon particles with more number of active surface sites for the adsorption and the saturation occurs as a result of non-availability of dye molecules for adsorption.

Adsorption Isotherms: The data obtained from equilibrium studies were analyzed according to Langmuir and freundlich adsorption isotherms. The langmuir and freundlich equations are commonly used to describe adsorption isotherms at a constant temperature for water and waste water treatment applications. The distribution of dyes between the solid-solution interface equations has been described by the Langmuir equation [15]. The well known expression of the Langmuir model is given by equation no (1).

$$q_e = Q_o bc_e / (1+bc_e) \quad 1$$

Whereas q_e (mg/g) and C_e (mg/g) are the amounts of adsorbed dye per unit weight of adsorbent and unadsorbed dye concentration in solution at equation respectively. Q_o is the maximum amout of the dye bound per unit weight of adsorbent to form a complete monolayer on the surface at high C_e and b is a constant related to the affinity of the binding sites (L/mg).



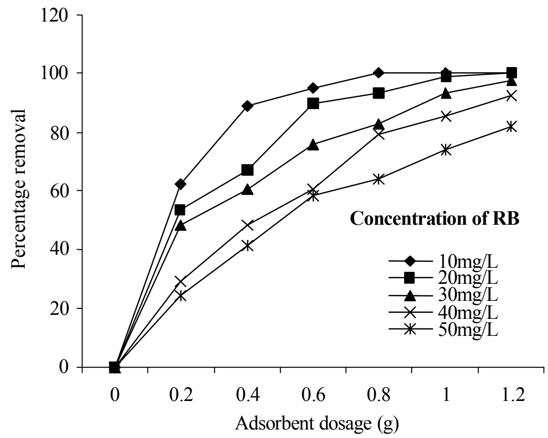


Fig. 4: Effect of carbon dosage on (a) Reactive orange 107, (b) Reactive black 5 adsorption onto carbon.

Table 4: Langmuir and Freundlich model constants

	Langmuir model						Freundlich model	
Dye	Q_o(mg/g)	b, L/mg	R^2	C_0, mg/L	R_L	K_f, L/mg	n	R^2
				10	0.342			
				20	0.207			
Reactive orange	21.27	0.192	0.9943	30	0.148	1.3053	3.8643	0.8280
				40	0.115			
				50	0.094			
				10	0.364			
				20	0.222			
Reactive black	523.92	0.175	0.9927	30	0.159	1.2200	3.5871	0.7467
				40	0.125			
				50	0.103			

Table 5: Comparison of the Q_o values for various adsorbents

Dyes	Adsorbent	Q_o(mg/g)	Reference
Reactive black5	Pericarp of Gloriosa superba	23.92	This work
	Biomass fly ash	4.38	Pengthamkeerati *et al.*, 2008
	Coal fly ash (high lime)	7.94	Eren *et al.*, 2006
	Powdered activated carbon	58.8	Eren *et al.*, 2006
	Bagasse fly ash	16.42	Rachakornkij *et al.*, 2004
	Modified zeolite	60.6	Ozdemir *et al.*, 2004
	Modified clay(sepiolite)	120.5	Ozdemir *et al.*, 2004
	Brown seaweed (acidTreated)	73.2	Vijayaraghavan and Yun, 2008
	Activated carbon (300-500_m)	434	Al-Degs *et al.*, 2000
	Activated carbon (500-600_m)	333	Al-Degs *et al.*, 2000
	Activated carbon (600-700_m)	278	Al-Degs *et al.*, 2000
Reactive orange 107	Pericarp of *Gloriosa superba*	21.27	This work
Reactive Yellow 176	Biomass fly ash	3.65	Pengthamkeerati *et al.*,2008
	Modified zeolite	88.5	Ozdemir *et al.*, 2004
	Modified clay (sepiolite)	169.1	Ozdemir *et al.*, 2004
Reactive Yellow 2	Activated carbon (300-500_m)	209.4	Al-Degs *et al.*, 2008
Reactive Yellow 64	Calcined alunite	236	Ozacar and sengil, 2003
Reactive Yellow 64	Alunite	5	Ozacar and sengil, 2003
Sunset Yellow	Powdered peanut hull	13.99	Gong *et al.*, 2005
Reactive yellow208	Hydrotalcite	47.8	Lazaridis *et al.,* 2003

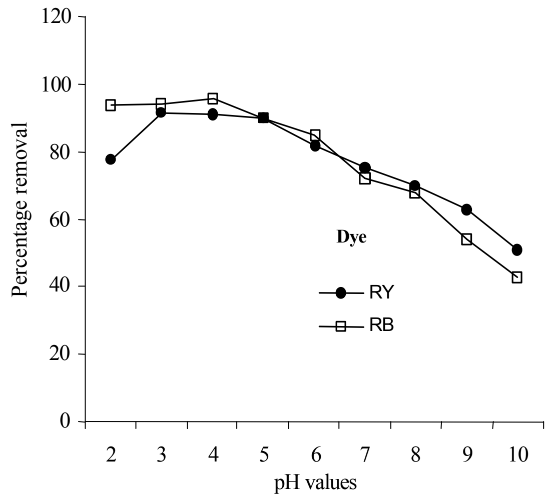


Fig. 5: Effect of pH on Reactive orange 107 and Reactive black 5 dye adsorption onto carbon

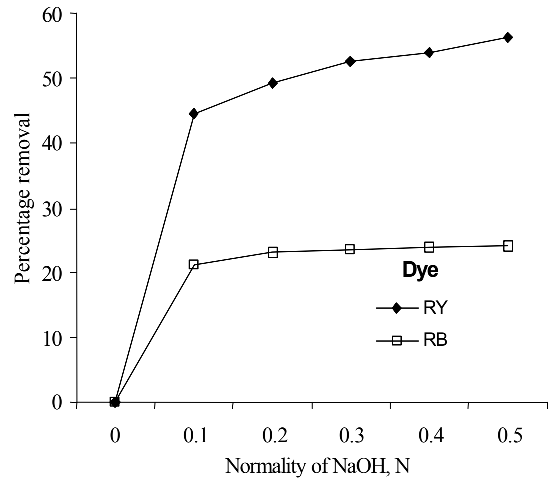


Fig. 6: Desorption studies for Reactive orange 107 and Reactive black 5 adsorption

The empirical Freundlich equation based on sorption into a heterogenous surface is given as

$$q_e = K_F C_e^{1/n}$$

Whereas K_f and n are the freundlich constants for the system, which are indicators of adsorption capacity and intensity respectively [16].

The values of the freundlich and Langmuir parameters were obtained respectively from the linear correlation between the values of C_e/q_e and C_e and log q_e and log C_e (Table 4). The linear relationships were evidenced by the R^2 values (for the Langmuir model, 0.9943 and 0.9927 for Reactive orange 107, reactive black 5, respectively; for the fruendlich model, 0.828 and 0.7467 for Reactive orange 107, reactive black 5 respectively) (Table 4). This indicates the applicability of the 2 adsorption isotherm and the monolayer coverage on the adsorbent surface. But for the RB 5, it can be seen that the Langmuir model ($R^2 = 0.7467$), in agree with the adsorption of vertigo navy marine and reactive dye on activated carbon [17, 18].

The Q_o from Langmuir isotherm indicates that the adsorption capacity of PGS was greater for the RB 5 (23.92 mg/g) than the RO 107 (21.27mg/g). The observed R_L values indicate favorable adsorption of the RB5 and RO 107 on PGS ($0<R_L<1$). Comparison of the Q_o obtained from this study and other adsorbents was presented in table 5.

Effect of pH on Reactive Orange 107 and Reactive Black 5 Removals: Adsorption of dye decreased with increasing pH. Lower adsorption of both dyes at alkaline pH was probably due to the presence of excess of hydroxyl ions competing with the dye anions for the adsorption sites (Figure 5).

Desorption Studies: Regeneration of the adsorbent may take the treatment more economical. Attempts were made to degenerate color from the dye laden carbon using various strengths of NaOH (0.1-0.6N). The percent desorption increased with increasing NaOH concentration in the aqueous medium (Figure 6) and attained a maximum desorption at 0.6N NaOH solution. The effect of percentage desorption was inversely correlated to pH effect, indicating that ion exchange was probably the major mode of adsorption process. Similar results were observed for the adsorption of Congo red by coir pith carbon [5].

CONCLUSIONS

The capability of PGS for removing Reactive orange 107, reactive black 5 dyes was examined, including equilibrium and kinetic studies. Based on the experimental data, PGS had higher dye adsorption efficiency on Reactive Black 5 than Reactive orange 107. The Langmuir and freundlich isotherm models were used to investigate the adsorption capacity of Reactive orange 107, reactive black 5 dyes were found to be 21.27 and 23.92 mg/g respectively. The suitability of first and second order kinetic models for the sorption of both dyes was also discussed. It was decided that the adsorption kinetics of both adsorbents obeyed the second order adsorption model. Pericarp of *Gloriosa superba* is an agricultural waste after the seeds have been used for medicinal properties. Thus as a low-cost adsorbent, it has potential application of pericarp carbon for dye removal due to high availability, disposed problem and also higher adsorption capacity at lower concentration.

REFERENCES

1. O'Mahony. T., E. Guibal and J.M. Tobin, 2002. Reactive dye biosorption by Rhizopus arrhizus biomass, Enzyme Microbiol. Technol., 31: 456-463.
2. Aksu, Z.C. and S.S. Cagatay, 2006. Investigation of biosorption of Gemazol Turquoise Blue-G reactive dye by dried Rhizopus arrhizus in batch and continuous systems. Separation and Purification Technol., 48: 24e35.
3. Naveen Prasad, R., S. Viswanathan, J. Renuka Devi, Johanna Rajkumar and N. Parthasarathy, 2008. Kinetics and Equilibrium Studies on Biosorption of CBB by Coir Pith. American-Eurasian J. Scientific Res., 3(2): 123-127.
4. Abedi, M. and Z. Bahreini, 2010. Preparation of Carbonaceous Adsorbent from Plant of Calotropis Gigantea by Thermo-Chemical Activation Process and its Adsorption Behavior for Removal of Methylene Blue. World Applied Sciences J., 11(3): 263-268.
5. Namasivayam, C. and O. Kavita, 2002. Removal of congo red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste. Dyes Pigments, 54: 47-58.
6. Sugunadevi, S.R., M. Sathishkumar, K. Shanthi, K. Kadirvelu and S. Pattabhi, 2002. Removal of Direct T-blue R from aqueous solution onto carbonised sugarcane baggase waste. Indian J. Environ. Protection, 22: 500-505.
7. Deepa, K.K., M. Sathishkumar, A.R. Binupriya, G.R. Murugesan, K. Swaminathan and S.E. Yun, 2006. Sorption of Cr(VI) from dilute solutions and wastewater by live and pretreated biomass of *Aspergillus flavus*. Chemosphere, 62: 833-840.
8. Sathishkumar, M., A.R. Binupriya, and D. Kavitha 2007. Kinetic and isothermal studies on 2, 4-dichlorophenol by palm pith carbon. Bioresour Technol., 98: 866-873.
9. Sathishkumar, M., A.R. Binupriya., D. Kavitha and R. Selavakumar, 2009. Adsorption potential of maize cob carbon for 2, 4-dichlorophenol removal from aqeous solutions: Equillibrium, kinetics and thermodynamics modeling. Chemical Engineering J., 147: 265-271.
10. Madhavakrishnan, S., K. Manickavasagam, K. Rasappan, P.S. Syed shabudeen, R. Venkatesh. and S. Pattabhi, 2008. Ricinus Communis Pericarp Activated Carbon Used as an Adsorbent for the Removal of Ni(II) From Aqueous Solution. E. J. Chemistry, 5(4): 761-769.
11. Lagergren, B. and V.P. Svenka, 1898. Zur theorie der sogenannten adsorption geloester stoffe, Kungliga Svenska Vetenskapsakad. Hand., 24: 1-39.
12. Ho, Y.S. and G. McKay, 1998. Kinetic models for the sorption of dye from aqueous solution by wood. Trans. Chem., 76B: 183-191.
13. McKay, G., J.F. Porter and G.R. Prasad, 1999. The removal of dye colours from aqueous solutions by adsorption on low-cost materials. Water Air Soil Pollut., 114: 423-438.
14. Nanthakumar, K., K. Karthikeyan and P. Lakshmanaperumalsamy, 2009. Investigation on Biosorption of Reactive Blue 140 by Dead Biomass of Aspergillus niger HM11: Kinetics and Isotherm Studies. Global J. Biotechnology and Biochemistry, 4(2): 169-178.
15. Namasivayam, C. and R.T. Yamuna, 1995. Waste biogas residual slurry for the removal of Pb(II) from aqueous solution and radiator manufacturing industry wastewater. Bioresource Technol., 5: 125-131.
16. Aksu, Z. and D. Dönmez, 2003. A comparative study on the biosorption characteristics of some yeasts for Remazol Blue reactive dye. Chemosphere, 50: 1075-1083.
17. Janos, P., H. Buchtova and M. Ryznarova, 2003. Sorption of dyes from aqueous solutions onto fly ash. Water Res., 37: 4938-4944.
18. Gupta, G.S., G. Prasad and V. N. Singh, 1999. Removal of chrome dye from aqueous solutions by mixed adsorbents: Fly ash and coal. Water Res., 24(1): 45-50.