RJC
http://www.rasayanjournal.com

RASĀYAN *J. Chem.*
Vol.2, No.4 (2009), 813-824
ISSN: 0974-1496
CODEN: RJCABP

ADSORPTION OF MALACHITE GREEN FROM AQUEOUS SOLUTION ONTO A WASTE AQUA CULTURAL SHELL POWDERS (PRAWN WASTE): KINETIC STUDY

T. Santhi[1*] , S. Manonmani [2.] , T.Smitha[1] , and K. Mahalakshmi[1]
[1] Department of Chemistry, Karpagam University,Coimbatore-641021, India.
[2] Department of Chemistry, PSG College of Arts and Science,Coimbatore-641014, India
E-mail:ssnilasri@yahoo.co.in

ABSTRACT

Prawn waste has become one of the most significant wastes in aquaculture, especially in Nagapattinum District, Tamil Nadu, India. A sample of raw (PR-Raw) and activated carbon (PR-Carbon) from prawn waste had been utilized as an adsorbent for uptake of cationic dye(i.e., malachite green (MG)) from aqueous solution at 28 ^{0}C. The effects of variousExperimental parameters (e.g., contact time, dye concentration, adsorbent dose, particle size and pH) were investigated and optimal experimental conditions were ascertained. The value of initial pH 7 for PR-Carbon and pH 8 for PR-Raw, could be remove MG effectively. The equilibrium adsorption capacity of MG onto the PR-Carbon is significantly larger than those onto the PR-Raw. It was further found that Langmuir, Freundlich and Dubinin – Radushkevich isotherms were useful for describing the equilibrium of adsorption system. The biosorption processes followed the Pseudo –first order rate kinetics. The nature of the rate-limiting step in a batch system can also be assessed from the intra-particle diffusion kinetic modeling. The parameters (amount of dye adsorbed at equilibrium) of the model obtained in the present work were significantly in line with the adsorption process parameter (i,e., initial dye concentration).

Key Words: Prawn waste, bioadsorption, malachite green, kinetic modeling, isotherm.

INTRODUCTION

Dyes and pigments are widely used, mostly in the textiles, papers, plastics, food and cosmetic industry to color products. Organic dyes are an integral part of many industrial effluents and demand an appropriate method to dispose them off. Most commercial dyes are chemically stable and are difficult to be removed from wastewater[1]. At present, more than 10,000 dyes have been effectively commercialized[2]. The release of colored Wastewater from these industries may present an eco-toxic hazard and introduce the potential danger of bioaccumulation, which may eventually affect man through the food chain. There are various conventional methods of removing dyes from waters. Among these methods, adsorption is by far the most versatile and widely used method because of its low cost, ease of operation. A number of agricultural waste and by- products of cellulose origin have been studied for their capacity to remove dyes from aqueous solutions, such as peanut hulls[3], maize bran[4], sawdust[5], sugar beet pulp[6], crab shell[7], cornstarch[8], rice husk[9], chitin[10], orange waste[11], lemon peel[12], granular kohlrabi peel[13], raw barley straw[14] , eggshell[15], aquacultures shell powders[16]. Due to increase of shellfish consumption in the past decade, the derived shell from the aquaculture farming and commercial market has become one of the most significant wastes in Nagapattinam, Tamil Nadu. Most of this was locally dumped into public waters and lands without proper treatment, causing a serious odor problem as a result of the remaining attached to the shellfish.

In this study, low cost locally available prawn waste was studied for its potential use as an adsorbent for removal of a cationic dye (MG) from aqueous solution. Factors affecting adsorption, such as, initial dye concentration, pH, contact time and adsorbent dose, were evaluated. The equilibrium of adsorption was modeled by using the Langmuir, Freundlich and Dubinin – Radushkevich isotherms models, the kinetic parameters and intraparticle diffusion were also then determined for the malachite green - prawn waste system. Results of this study will be useful for future scale up using this prawn waste material as a low- cost adsorbent for the removal of cationic dyes. These adsorbents can be used once, and then disposed as a fermentation substrate to produce fertilizer for vegetable cultivation.

MATERIALS AND METHODS

Preparation of the prawn waste adsorbent

The shell of prawn was obtained from an aquaculture farm in Nagapattinaum (Tamil Nadu). It was air- dried and powdered in a grinder. The dry biomass was crushed into granules, sieved to different particle sizes, and then preserved in desiccators for use (i,e.,PR- Raw). Air- dried and powdered prawn waste was soaked in concentrated H_2SO_4 for 12 hours and washed thoroughly with distilled water till it attained neutral pH and soaked in two percent $NaHCO_3$ overnight in order to remove any excess acid present. Then the material was washed with distilled water and dried at 110 ± 2^0C. The dry biomass was crushed into granules, sieved to different particle sizes, and then preserved in desiccators for use (i,e.,PR- carbon).

Preparation of cationic dye solutions

The cationic dye used as target adsorbate in the present study is malachite green, in commercial purity, which was purchased from s.d.Fine Chemicals, Mumbai, India, and used without further purification. The dye stock solutions were prepared by dissolving accurately weighted dyes in distilled water to the concentration of 500 mg / L. The experimental solutions were obtained by diluting the dye stock solutions in accurate proportions to different initial concentrations.

Experimental methods and measurements

Bioadsorption experiments were carried out in a rotary shaker at 150 rpm using 250ml- shaking flasks containing 50 ml of dye solutions at different concentrations and initial pH values of dye solutions. The initial pH values of the solutions were previous adjusted with 0.1M HCL or 0.1 M NaOH using a DEEP VERSION model (EI) pH meter. The adsorbent (0.1 g) was added to each flask, and then the flasks were sealed up to prevent any change of volume of the solution during the experiments. After shaking the flasks for a predetermined time intervals, the samples were withdrawn from the flasks and the dye solutions were separated from the adsorbent by filtration after centrifugation. The pH values of the separated dye solutions were again measured for examining their change. Dye concentrations in the supernatant solutions were estimated by measuring absorbance at maximum wavelengths of dye with a Systronic Spectrophotometer-104. The amounts of dyes adsorbed by the biomass were calculated using the following equation:

$$q = (C_0 – C_e) V/W \qquad (1)$$

Where q (mg/g) is the amount of dye adsorbed by the biomass, C_0 and Ce (mg/L) is the initial and equilibrium liquid –phase concentration of dye, respectively, V (L) the initial volume of dye solution, and W (g) the weight of the biomass.

The effect of each parameter was studied by fixing the values of other parameters. The experiments were conducted with duplicate and the negative controls (with no adsorbent) to ensure that adsorption was by the prawn waste biomass and not by the container.

RESULTS AND DISCUSSION

Influence of initial pH

The effect of initial pH on bioadsorption percentage of dyes was examined over a range of pH values from 2 to 10 and the results are presented in Fig. 1. As elucidated in Fig. 1, the dye removal was minimum at pH 2 for both adsorbents. The dyes adsorbed increased as the pH was increased from 2 to 7 for PR-Carbon and from 2 to 8 for PR-Raw. Then, beyond pH 7 and 8 there was no notable change. For this reason, pH 7 and 8 was selected for future experiments for PR-Carbon and PR-Raw used as adsorbent.

After adsorption experiments, it was found that at low pH and at high pH, the dye become protonated, the electrostatic repulsion between the protonated dyes and positively charged adsorbent sites results in decreased adsorption. Higher adsorption at pH 7 and 8 may be due to increased protonation by the neutralization of the negative charges at the surface of the adsorbent; which facilitates the diffusion process and provides more active sites for the adsorbent.

Influence of initial dye concentration

The influence of dye concentration on bioadsorption of dye is shown in Fig 2.when the dye concentration was increased from 25 to 200 mg/L, the percentage of dye adsorbed was between 80.32 % and 30.43%(PR-Carbon), 66.91 % and 10.88% (PR- Raw).

Adsorption Isotherms

The equilibrium adsorption isotherm is fundamental in describing the interactive behavior between adsorbate and adsorbent, and is important in the design of adsorption systems.The linearised form of the Langmuir equation[17] is as follows

$$C_e / q_e = 1 / (\mathbf{a} Q_m) + C_e / Q_m \qquad (2)$$

Where C_e (mg/L) is the concentration of the dye solution at equilibrium, q_e (mg/g) is the amount of dye adsorbed at equilibrium, Qm is the sorbent binding capacity, that is, the maximum sorption upon complete saturation of adsorbent surface and $\mathbf{a}$ is binding constant, that is, related to the adsorption/desorption energy. It is well known that the Langmuir equation is intended for a homogeneous surface. A good fit of this equation reflects monolayer adsorption[18].The Q_m and $\mathbf{a}$ values are calculated from the slopes ($1/Q_m$) and intercepts ($1/ \mathbf{a} Q_m$) of linear plots of C_e / q_e versus C_e, that is shown in the Fig. 3a and 3b. From the results in Table 1, it could be concluded that the Langmuir model did not give a good fit to the sorption process when compared to the other isotherms tested. This is also confirmed from the negative values obtained for Langmuir constants shown in Table 1.The linearised form of the Freundlich equation[19] is as follows:

$$\ln Q_e = \ln K + (1/n) \ln C_e \qquad (3)$$

Where Q_e is the amount of dye adsorbed at equilibrium, Ce is the concentration of the dye solution at equilibrium and 1/n are empirical constant and indicate adsorption capacity and intensity, respectively. The values of K and n determine the steepness and curvature of the Isotherm20. The Freundlich equation frequently gives an adequate description of adsorption data over a restricted range of concentration, even though it is not based on the theoretical background. Apart from homogeneous surface, the Freundlich equation is also suitable for a multi-layer adsorption[21] . The values of 1/n , not less than unity is an indication that less significant adsorption takes place at low concentration but the increase in the amount adsorbed with concentration becomes more significant at higher concentration. The K values which are higher for the PR-Carbon confirms that the adsorption capacity of the PR- Carbon was greater than that of the PR-Raw. Their values were obtained from the intercepts (ln K) and slope (1/n) of linear plots of ln Q_e versus ln C_e, which is shown in the Fig. 4a and 4b.

The linearised form of the Dubinin-Radushkevich isotherm [22] is as follows:

$$\ln q_e = \ln q_m - B\ \varepsilon^2 \qquad (4)$$

Where B is a constant related to the mean free energy of adsorption per mol of the adsorbate $(\mathrm{mol}^2\,\mathrm{J}^{-2})$, q_m is the theoretical saturation capacity(mol g^{-1}) and ε is the Polanyi potential, Which is equal to RT ln (1+ $1/C_e$), where R (J $mol^{-1}K^{-1}$) is the gas constant and T (K) is the absolute temperature. Hence by plotting ln q_e versus ε,^{2} which is shown in the Fig. 5a and 5b, it is possible to obtain the value of q_m from the intercept and the value of B from the slope. Values of q_m and B are presented in Table 1. The constant B gives an idea about the mean free energy E (KJ mol^{-1}) of adsorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution and can be calculated from the relationship[23].

$$E = 1/\sqrt{2B} \qquad (5)$$

If the magnitude of E is between 8 and 16 KJ mol^{-1}, the adsorption process follows ion exchange, While for the values of E lesser than 8 KJ mol^{-1} , the adsorption process is of physical nature. High values of E of 24.7 ± 3.2 KJ mol^{-1} shows that strong chemical bond formation between adsorbate and adsorbent[24] . Since the value of E is 14.14 KJ mol^{-1} for PR-Carbon and 24.49KJ mol^{-1} for PR-Raw, the adsorption follows ion exchange mechanism for PR-Carbon and the adsorption follow chemisorptions mechanism for PR-Raw.

The Q_m and **a** values in the Langmuir equation, the k and 1/n values in the Freundlich equation, q_m and B values in Dubinin-Radushkevich isotherm, the correlation coefficients of these equations are given in the Table 1. We can conclude from the values of R^2 that Freundlich isotherm is the best followed by Dubinin- Radushkevich isotherm. The Langmuir isotherm would be said as not giving a good fit to the sorption process.

Effect of sorbent particle size

The effect of sorbent particle size on biosorption of dyes is shown in Fig. 6. The dyes adsorbed increased as the sorbent particle size decreased. It was suggested that the increase in- sorption depended on the large external surface area for small particles; this removes more dye in the initial stages of the sorption process than the large particles. This criteria was considered vital in choosing the ideal particle size as 125-250 mμ, furthermore smaller particles than this tend to clog the column during industrial applications.

Effect of adsorbent Dose

The adsorption of the dyes on carbon was studied by varying the concentration of the activated carbon from prawn waste biomass (0.1- 0.4 g/mL). The percentage of adsorption increased as the adsorbent concentration increased shown in Table 2. The increase in the percent removal of dyes with the increase in adsorbent dosage is due to the availability of larger surface area with more active functional groups at higher adsorbent dosages.

Adsorption kinetics

The chemical kinetic describes reaction pathways, along times to reach the equilibrium whereas chemical equilibrium gives no information about pathways and reaction rates. In order to investigate the mechanism of adsorption various kinetic models have been suggested. In recent years, adsorption mechanisms involving kinetics-based models have been reported. In this study , some of these models were investigated to find the best fitted model for the experimental data obtained.

Adsorption kinetic data of MG are analyzed using the Lagergren pseudo-first –order rate equation :

$$\lg (q_e - q_t) = \lg q_e - k_{ad}\, t / 2.303 \qquad (6)$$

Where q_e and q_t (mg /g) refer to the amount of dye adsorbed at equilibrium and time t (min), respectively, and k_{ad} is the rate constant. The rate constant k_{ad} could be calculated from the slopes of the linear plots of lg ($q_e - q_t$) verses t. The Lagergren plots of dye biosorption are shown in Fig. 7.

The second order kinetic model[25] can be represented as:

$$t/q_t = 1/k_2q_e^2 + 1/q_e \qquad (7)$$

where k_2 is the rate constant of second order adsorption. Values of k_2 and q_e were calculated from the plots of t/q vs t (Fig. 8).

Table 3 showed that the correlation coefficients for the pseudo-first-order rate kinetic Plots were above 0.9239 for PR-Carbon and 0.806 for PR-Raw. These results indicate that the adsorption process generally follows the first order kinetic model.

Intra- particle diffusion

If the intra –particle diffusion is involved in the adsorption processes, then the plot of thesquare root of time versus the uptake (q_t) would result in a linear relationship and the intraparticle diffusion would be controlling step if this line passed through the origin. When the plots do not pass through the origin, this indicative of some degree of boundary layer control and this further shows that the intraparticle diffusion is not the only rate controlling step, but also other processes may control the rate of adsorption[26].

As shown in the Fig. 9, the slope of the first linear portion characterizes the rate parameter corresponding to the intraparticle diffusion, whereas the intercept of this portion is proportional to the boundary layer thickness. The R^2 value for this diffusion model was 0.9273 for PR- Carbon and 0.9239 for PR-Raw. This indicates that the adsorption of MG onto PR-Carbon and PR-Raw can be followed by interaparticle diffusion model. However, the lines do not pass through the origin(the plots have intercept of -0.561 for PR-Carbon and -4.5358 for PR-Raw), indicating that interaparticle diffusion is not the only rate limiting mechanism and that some other mechanisms also play an important role. Surface adsorption and interaparticle diffusion were likely to take place simultaneously, both the processes controlling the kinetics of dye – adsorbent interaction[27].

CONCLUSION

The present study shows that the natural shellfish shells , an abundant low cost prawn waste, can be used as adsorbent for the removal of malachite green dye from aqueoussolutions. The amount of dye adsorbed was found vary with initial pH, adsorbent dose, dye concentration and contact time. The adsorption equilibrium data were found to fit the D-R and Freundlich isotherm, indicating not a monolayer adsorption on a homogenous surface. Lagergren pseudo-first –order, second order and intra –particle diffusion models can be used to predict the adsorption kinetics. The adsorption mechanisms were deduced with the help of mean free energy .

REFERENCES

1. M.M .Nassar and Y.H. Magdy, . *Chemical Engineering Journal*, **66 ,** 223-226(1997).
2. R..Gong , M.Li,C.Yang, Y.Sun and J.Chen,. *Journal of Hazardous Materials* ,**121**, 247-250. (2005)
3. P. Brown , I.A. Jefcoat, D. Parrish, S. Gill and E.Graham , *Advaces in Environmental Research*, **4** , 19-29(2000).
4. K. K.Singh, M. Talat and S. H.Hasan , *Bioresource Technology* , **97,** 2124-2130(2006).
5. V. C .Taty-Costodes, H. Fauduet, C.Porte and A.Delacroix, *Journal of Hazardous .Materials*, **B105,** 121-142(2003).
6. Z. Reddad, C. Gerente, Y.Andres and P.L. Cloirec, *Enviromental science and Technology*, **36,** 2067-2073 (2002).
7. K. Vijayaraghavan, K. Palanivelu and M. Velan, *Bioresource Technology*, **97,**1411-1419(2006).
8. D.K.Kweon, J.K.Choi, E.K.Kim, S.T.Lim, *Carbohydrate Polymers*, **46**, 171-177(2001).

9. U.Kumar and M. Bandyopadhyay, *Bioresource Technology* , **97**, 104-109(2006).
10. K. N . Ghimire, K. Inoue, T.Miyajima, K.Yoshizuka and T. Shoji,*Chitin and Chitosan Research*, **7 (2),** 61-68(2001).
11. R. P .Dhakal , K. N. Ghimire, K.Inoue, M.Yano and K.Makino, *Separation and Purification Technology*, **42**, 219-225(2005).
12. K. Vasanth Kumar, *Dyes and Pigments* ,**74,** 595-597(2007).
13. Renmin Gong, Xiaoping Zhang, Huijun Liu, Yingzhi Sun and Birong Liu, *Bioresource Technology* , **98,**1319-1323(2007).
14. M .Husseien, A. A. Amer, Azza EI- Maghraby and A.Nahla, *Journal of Applied sciences Research*; **3** (11): 1352-1358(2007).
15. Nuttawan Pramanpol and Nuttakan Nitayapat,, *Kasetsart Journal : Natural Science*, **40,** 192-197(2006).
16. Wen-Tien Tsai., Huei-Ru Chen., Kuan- Chi Kuo., Chia-Ying Lai., Tu- Cian Su., Yuan- Ming Chang and Jwu-Maw Yang, *Journal of Environmental Engineering Management*, **19(3)** , 165-172(2009).
17. I.. Langmuir., *Journal of American Chemical .Society* , **40(9) ,**1361-1403(1918).
18. Teng, Hsisheng and Hsieh, Chien-To, *Industrial and Engineering Chemistr Research* ; 37: 3618-3624(1998) .
19. H.M.F Freundlich, *Zeitschrift für Physikalische Chemie*; **57 A** ,385-470(1906).
20. Akgerman, Aydinand Zardkoohi, Minoo, *Journal of Chemical Engineering Data*, **41(2)**, 185-187(1996).
21. Juang, Ruey- Shin., WU, Feng-Chin and Tseng., *Journal of Chemical Engineering Data;* **41(3**), 487-492(1996).
22. T.K .Dan , *Indian Coconut Journal*, **23(11**), 12-19(1993).
23. A.S . Ozcan, B.Erdom and A. Ozcan, *Colloids and Surface A*, **266(1-3)**,73- 81(2005).
24. S.M. Hasany , M.M. Saeed and M. Ahmed, *Talanta*, **54(1)**, 89-98(2001).
25. G.Blanchard, M. Maunaye and G. Martin, *Water Research*,**18(12)**, 1501-1507(1984).
26. G.Crini, , H.N, Peindy, F. Gimbert and C. Robert, *Separation and Purification Technology*, **53,** 97-110(2007).
27. S .Alzaydien. Atef , *American Journal of Environmental Sciences*; **5 (3),**197-208(2009).

Table-1:The Q_m , a values in the Langmuir equation, the K and 1/n values in Freundlich equation, q_m and B values in Dubinin-Radushkevich isotherm, R^2 the correlation coefficients of equations.

	Langmuir			Freundlich			Dubinin-Radushkevich		
	Q_m (mg/g)	a	R^2	K	1/n	R^2	q_m	B	R^2
PR-Carbon	9.166	0.0166	0.5632	4.465×10^{-3}	2.348	0.6027	50.31	0.0001	0.5699
PR-Raw	3.093	0.0127	0.8443	6.909×10^{-5}	3.042	0.7685	33.204	0.0003	0.5961

Table-2: Effect of adsorbent dosage on biosorption of dye (dye concentration: 100mg/L; contact time: 1h and 30minutes; pH: 7 for PR-Carbon, pH: 8 for PR-Raw; particle size: 125-250 mμ)

Adsorbent concentration (mg/L)	Dye adsorbed (%)	
	PR-Carbon	PR-Raw
100	55.55	32.79
200	61.05	40.97
300	77.38	67.19
400	87.97	74.3

Table-3: Comparison of first order and second order adsorption rate constant and the correlation coefficients of equations

First order kinetic model						Second order kinetic model					
_PR-Carbon			PR-Raw			PR-Carbon			PR-Raw		
Kad	q_e	R^2	Kad	q_e	R^2	k	q_e	R^2	k	q_e	R^2
0.0235	1.399	0.9239	0.0193	1.4043	0.806	0.0288	1.5249	0.822	0.0215	5.6635	0.2892

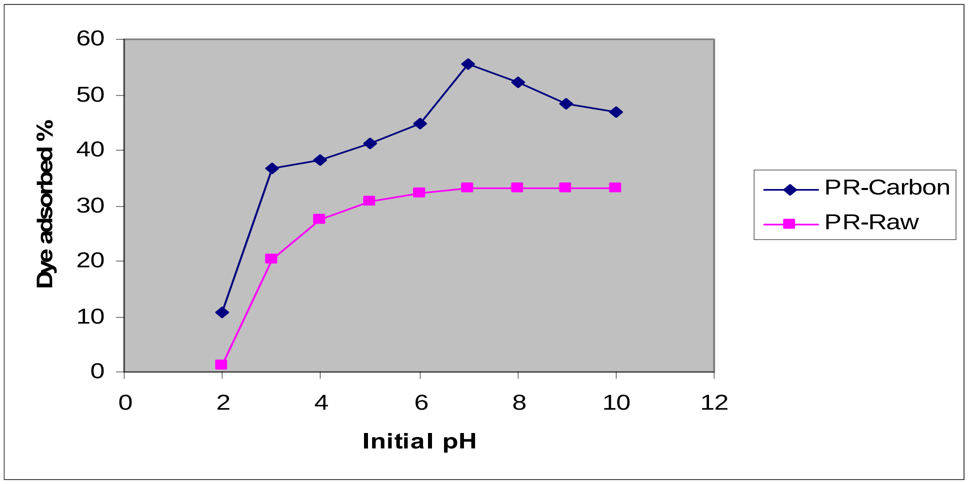

Fig-1: Influence of initial pH on bioadsorption of MG by PR-Carbon and PR-Raw (adsorbent dose: 100mg/50ml; particle size: 125-250mµ; contact time: 1h and 30minutes; dye concentration: 100mg/L)

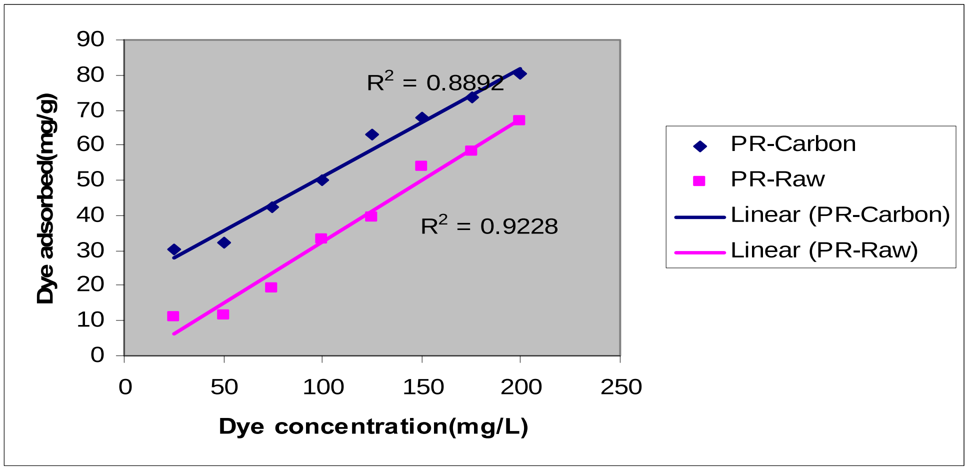

Fig.-2: Influence of dye concentration on bioadsorption of MG by PR-Carbon and PR-Raw (adsorbent dose: 100mg/50ml; particle size: 125-250mµ; contact time: 1h and 30minutes; pH: 7 for PR-Carbon, pH8 for PR-Raw).

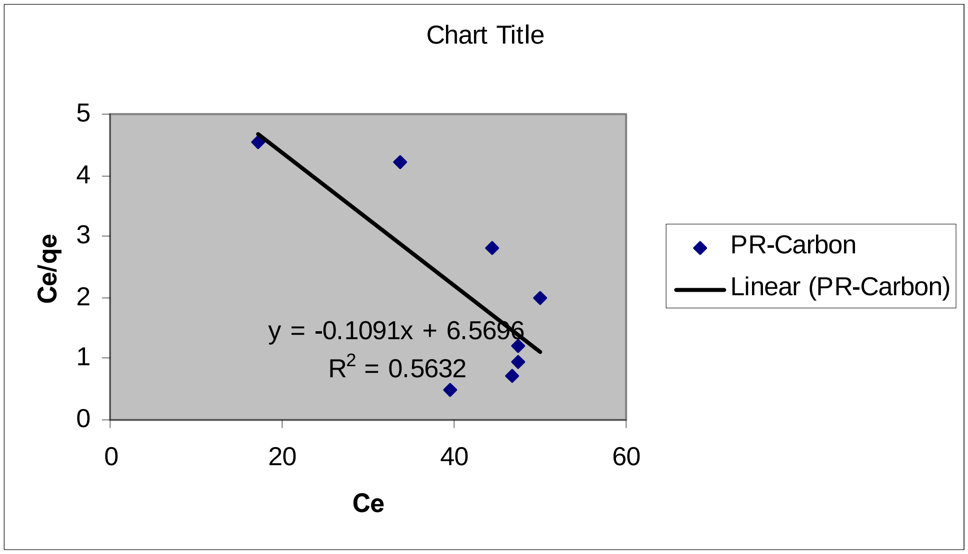

Fig.-3a: Langmuir plots for the adsorption of MG onto PR-Carbon

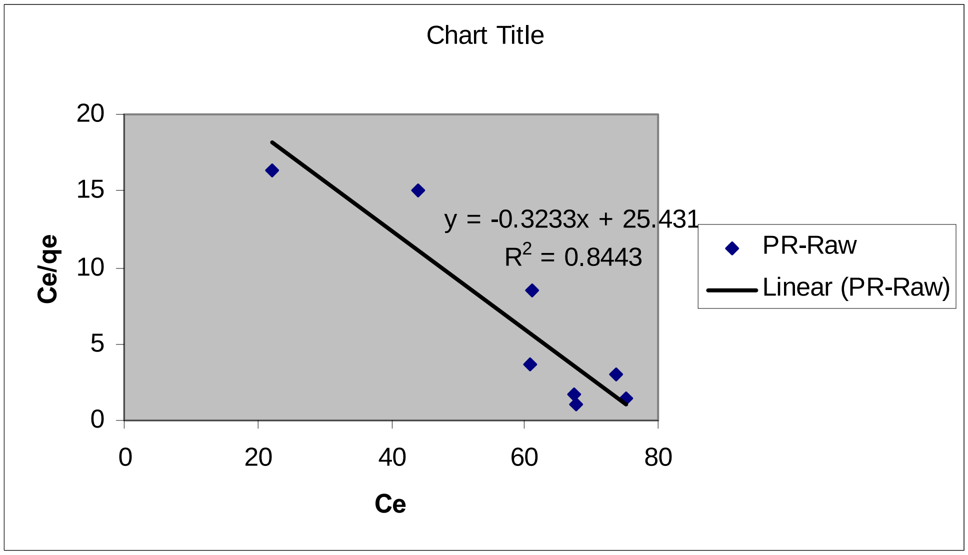

Fig.-3b: Langmuir plots for the adsorption of MG onto PR-Raw

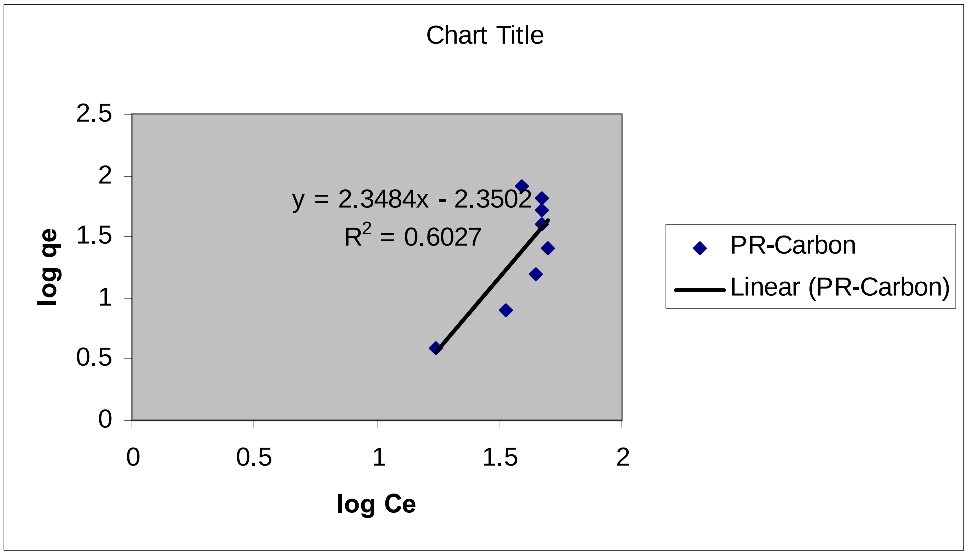

Fig.-4a: Freundlich plots for the adsorption of MG onto PR-Carbon

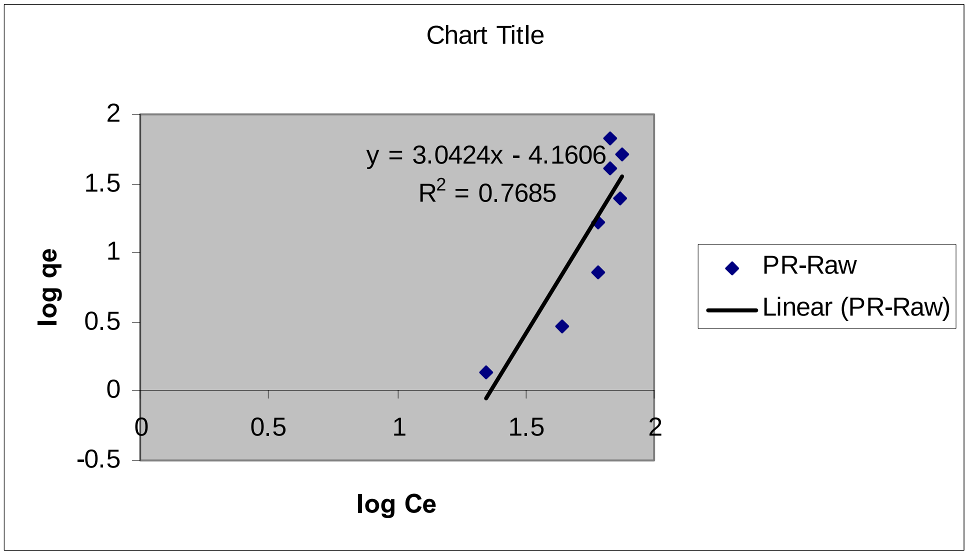

Fig.-4b: Freundlich plots for the adsorption of MG onto PR-Raw

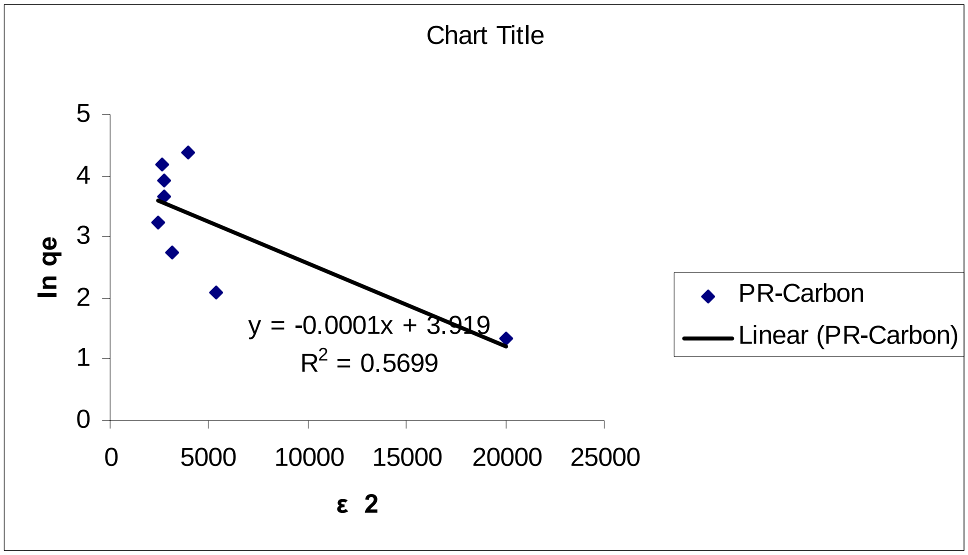

Fig.-5a: Dubinin-Radushkevich isotherm plots for the adsorption of MG onto PR-Carbon

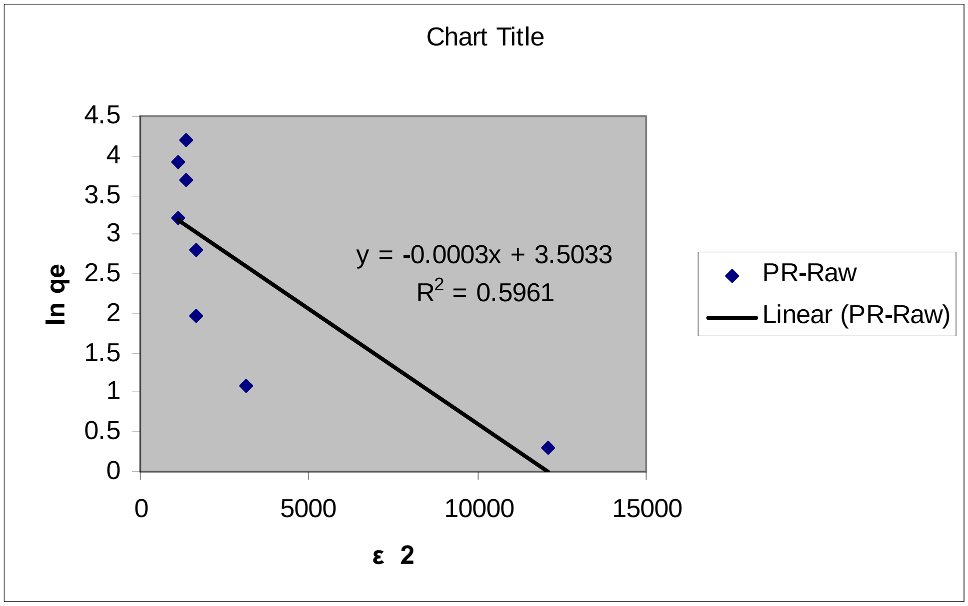

Fig.-5b: Dubinin-Radushkevich isotherm plots for the adsorption of MG onto PR-Raw

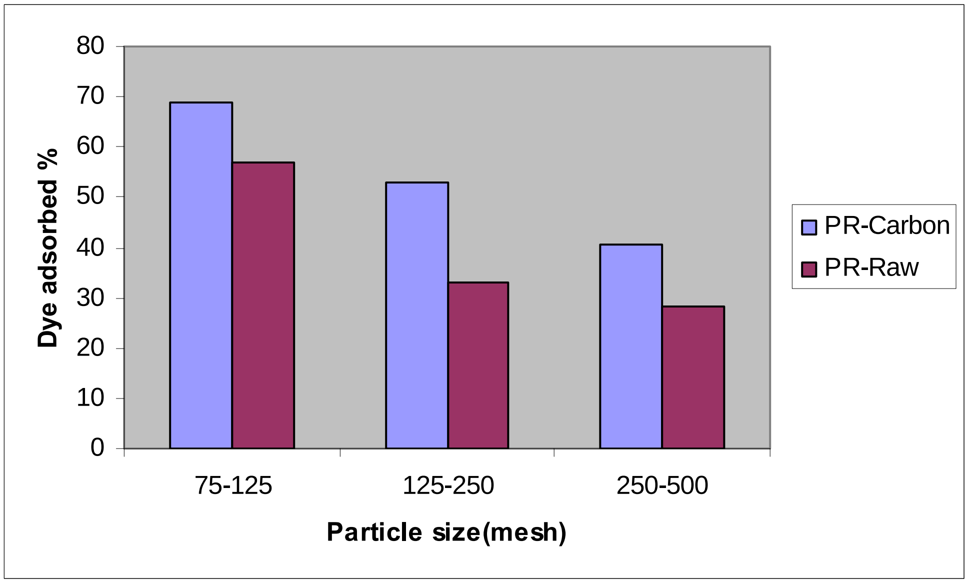

Fig.-6: Effect of particle size on bioadsorption of MG by PR-Carbon and PR-Raw (adsorbent dose: 100mg/50ml; Dye concentration: 100mg/L; contact time: 1h and 30minutes; pH: 7 for PR-Carbon, pH8 for PR-Raw).

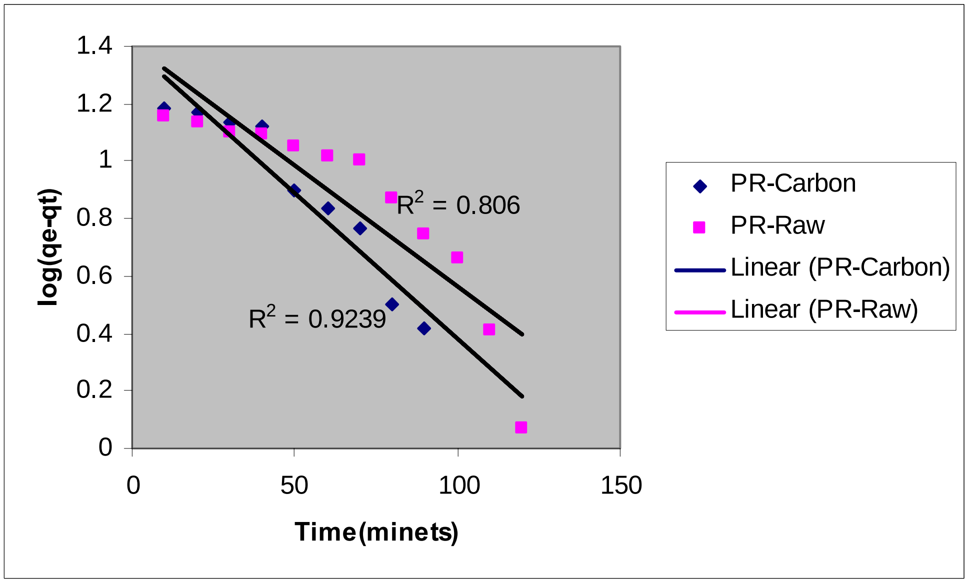

Fig.-7: First order plots for the bioadsorption of MG by PR-Carbon and PR-Raw (adsorbent dose: 100mg/50ml; Dye concentration: 100mg/L; contact time: 1h and 30minutes; pH: 7 for PR-Carbon, pH8 for PR-Raw).

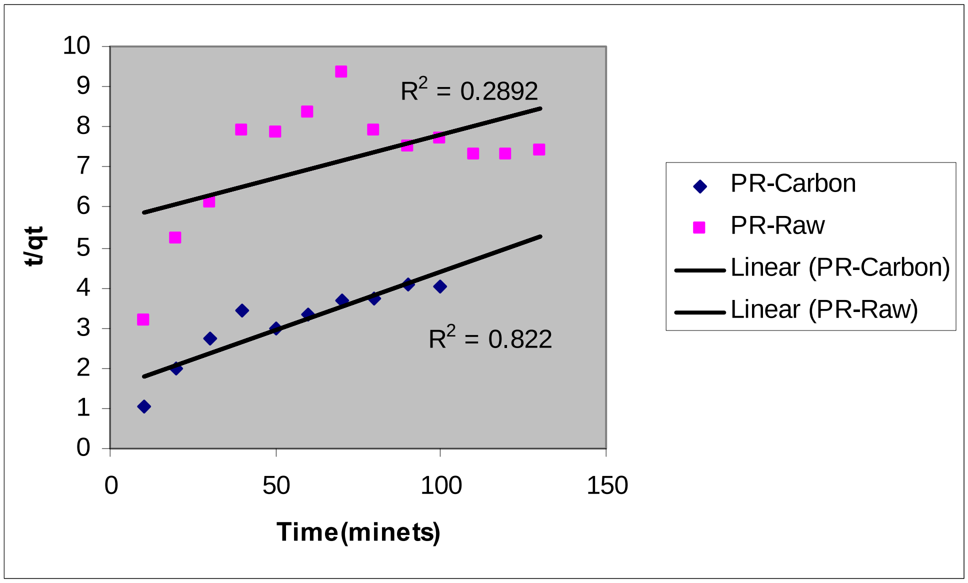

Fig.-8: Second order plots for the bioadsorption of MG by PR-Carbon and PR-Raw (adsorbent dose: 100mg/50ml; Dye concentration: 100mg/L; contact time: 1h and 30minutes; pH: 7 for PR-Carbon, pH8 for PR-Raw).

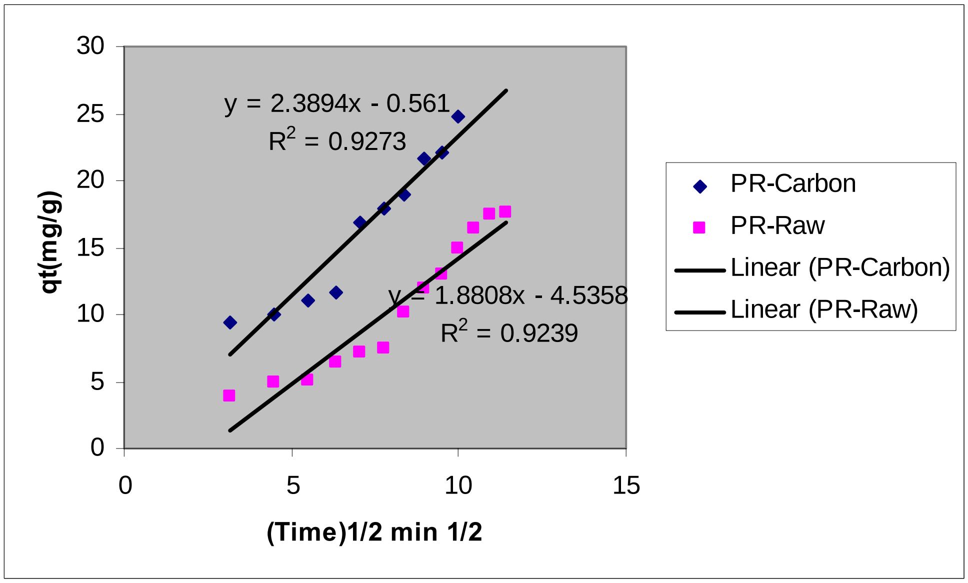

Fig.-9: Intraparticle diffusion kinetics for adsorption of MG onto PR-Carbon and PR-Raw biomass.(adsorbent dose: 100mg/50ml; Dye concentration: 100mg/L; contact time: 1h and 30minutes; pH: 7 for PR-Carbon, pH8 for PR-Raw).

(Received: 13 October 2009 Accepted: 25 October 2009 RJC-337)