Asian Journal of Chemistry; Vol. 29, No. 3 (2017), 535-540

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2017.20225

Equilibrium and Kinetic Studies of an Eco-Friendly Biosorbent for Removal of Procion Blue Dye from Aqueous Solutions: Water Lettuce (*Pistia stratiotes*) Dead Biomass

S. JEMIMAH[1,2,*] and S.R. BHEETER[2]

[1]Department of Chemistry, St. Joseph's College (Autonomous), Tiruchirappalli-620 002, India
[2]Department of Chemistry, St. Joseph's Institute of Technology, Chennai-600 119, India

*Corresponding author: Fax: +91 44 24503133; Tel: +91 44 24503132; E-mail: jemimahraj@gmail.com

Received: 1 August 2016; *Accepted*: 10 November 2016; *Published online*: 30 December 2016; AJC-18194

Procion blue dye has been removed from aqueous solution by dried biomass of water lettuce. The effect of experimental conditions such as pH, biosorbent dosage, initial dye concentration of procion blue, adsorption isotherm and adsorption kinetics of water lettuce were investigated. The morphology and elemental composition of water lettuce were analyzed by scanning electron microscope and energy dispersive spectroscope (SEM-EDS) respectively. Two kinetic models pseudo-first- and second-order equations were chosen to follow the adsorption process and the adsorption of procion blue followed pseudo-second-order kinetics. The experimental isotherm data were analyzed using Langmuir and Freundlich equations and found that the experimental data followed Langmuir isotherm suggesting homogenous, monolayer adsorption of the dye on the biomass surface. The results of the present study reveal that the dried water lettuce biomass is a promising low-cost sorbent for the removal of procion blue.

Keywords: Procion blue, Reactive blue 13, Adsorption, *Pistia stratiotes*, Water lettuce.

INTRODUCTION

The presence of dye contaminated aqueous streams arising from the discharge of untreated dye containing effluents into natural water bodies is one of the most important environmental issues. Dyeing industry effluents are one of the most problematic wastewaters to be treated for their high chemical oxygen demand, high biological oxygen demand, suspended solids, turbidity, toxic constituents and colour [1-3]. Dyes have a significant effect on the photosynthetic activity in aquatic life due to reduced light penetration and pose a threat to aquatic life [4]. Many dyes were known as carcinogens, such as benzidine and other aromatic components which might be reformed as a result of microbial metabolism [5]. Thus, colour removal is one of the most difficult challenges to be addressed by textile finishing, dye manufacturing, pulp and paper industries, among others. Numerous methods such as adsorption, coagulation, advanced oxidation, ultrafiltration, ion exchange, flocculation, biodegradation and membrane separation have been previously used in the removal of dyes from wastewater [5-12]. However these methods have significant disadvantages, including incomplete dye removal, requirement of expensive equipments, monitoring systems, high reagent or energy requirements and other waste products. The search for new technologies involving the removal of toxic metals from wastewaters has directed attention to the adsorption. Adsorption is a well known process and an efficient method for waste water treatment [2,13]. It is found to be superior to other methods in terms of it's capital cost, simplicity of operation design, the formation of harmless by products and does not require an additional pretreatment step before its application. Among the commonly used adsorbents, biosorbents are receiving interest lately because of its less hazardous nature, comparable low cost of application and high efficiency [13-16].

Aquatic plants are very promising materials to be used as biosorbents in wastewater treatments because they are an inexpensive source of biosorbent, are easily available and accessible in large quantities. *Eichhornia crassipes*, *Acalypha indica* and *Hydrilla verticillata* are few of the aquatic plants which have been reported earlier as effective biosorbents for both heavy metals and dye molecues [17-21]. These kind of aquatic plants are commonly associated with the purification capacity of water where they are present. Dead biomass is far more advantageous than live microorganisms in adsorption because it does not require a continuous supply of nutrients and may be stored or used for extended periods at room temperature without putrefaction occurring. The biomass can also be regenerated and reused in many cycles, which makes the removal of dyes from aqueous solution using dead biomass both safe and eco-friendly. This in turn creates a huge demand for new materials such as aquatic plants for waste water treatment. Water lettuce is among the world's most productive freshwater aquatic plants. Severe overgrowth of water lettuce can block gas exchange at the air-water interface, reducing the oxygen in the water and killing fish [22]. Water lettuce has been employed in the past for the remediation of few heavy metals and dye compounds [23].

Procion blue H-5R dye is a reactive dye, which is used for dyeing wool, cotton, nylon, silk and modified acrylics. In the present study an attempt has been made to use an eco-friendly and cost effective adsorbent – water lettuce for the treatment of Procion blue dye containing aqueous solution.

EXPERIMENTAL

Sodium hydroxide and hydrochloric acid used for pH studies were procured from Alfa Aesar and were of analytical grade. FT-IR was used for the determination of functional groups on the water lettuce surface. FT-IR was recorded using a Thermo IS5 FT-IR spectrophotometer. The dried biomass was ground well with KBr and compressed to form a pellet to obtain an absorption spectrum in the range of 4000-400 cm^{-1}. The surface morphology of water lettuce before and after adsorption was elucidated using scanning electron microscope. SEM-EDS was recorded using Hitachi 3000H SEM. The SEM was operated at an accelerating voltage of 5-10 kV. Gold sputtering was done on the surface of the samples prior to taking SEM to make the samples electrically conducting.

Preparation of adsorbent and adsorbate: Water lettuce plants, botanically called as *Pistia stratiotes* collected in a pond in Pondicherry, India were washed with deionized water, sun-dried and finely grounded. The dried biomass sample was sieved by passing through 70 mesh and retained in 80 mesh size. The sieved biomass was used for all the experiments.

Procion blue H-5R (Fig. 1, reactive blue 13, C.I. No. 181575; m.f. $C_{29}H_{16}ClN_7Na_4O_{14}S_4$, m.w. 866.06 and λ_{max} 444 nm) was purchased from Alfa Aesar. A stock solution of 10,000 mg/L of the reactive dye was prepared in a standard flask. The desired concentrations for various experiments were obtained by successive dilution using double distilled water.

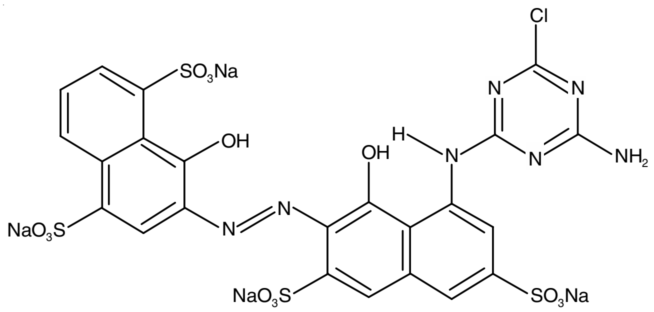

Fig. 1. Chemical structure of procion blue H-5R

Batch adsorption studies: Batch studies were conducted to find the optimum operating conditions for the treatment of procion blue present in aqueous solution. Different concentrations of procion blue dye solution were prepared. Dried biomass (in the range 0.1-0.5 g) of water lettuce was varied by weighing accurately and introducing 50 mL of procion blue dye solution into 250 mL Erlenmeyer flasks separately. These flasks were kept in a shaker (Scigenics Biotech Pvt. Ltd., Chennai, India) at 180 rpm at 30 °C. The samples were withdrawn at different time intervals of 0, 15, 30, 60, 90, 120, 150, 180 and 210 min and centrifuged at 12,000 rpm for 10 min to remove the biosorbent from the dye solution. The concentration of dye present in supernatant was measured using a UV spectrophotometer (Hitachi, U3210, Japan) at maximum wavelength. The dye uptake capacity q was determined using the following equation

$$q = [(C_o - C_e) \times V/W] \quad (1)$$

where C_o is the initial dye concentration (mg/L), C_e is the final dye concentration (mg/L), V is the volume of the sample (L) and W is the weighed biomass (g). The pH of the solution was varied in the range of 1-6 using 0.1 N HCl or 0.1N NaOH depending upon the required pH. The initial dye concentration varied between 25 to 200 mg/L by suitable dilution from 10000 mg/L dye stock solution. Samples were withdrawn at intervals to understand the rate at which equilibrium is reached. The absorbance measured was then converted to concentration and the dye uptake capacity q was assessed.

Equilibrium studies: The adsorption isotherm gives the relationship between the amount of adsorbate adsorbed by the adsorbent (q_{eq}) and the adsorbate concentration left in the solution (c_{eq}) after attainment of equilibrium at constant temperature. Valuable pieces of information regarding the affinity of the adsorbent for the adsorbate, adsorption mechanism and surface properties are deduced from the parameters of the equilibrium adsorption models. In this viewpoint, in present study, we studied the Langmuir and Freundlich models.

RESULTS AND DISCUSSION

FT-IR analysis: The FT-IR spectrum was obtained for biomass before and after procion blue dye adsorption process (Fig. 2). The FT-IR spectrum of water lettuce shows several absorption peaks corresponding to various functional groups. The band at 3403 cm^{-1} represents the presence of –OH group. The band observed at 2920 and 2852 cm^{-1} is assigned for asymmetric and symmetric vibrations of CH group. The bands at 1638 and 1419 cm^{-1} are attributed to the presence of –COO and

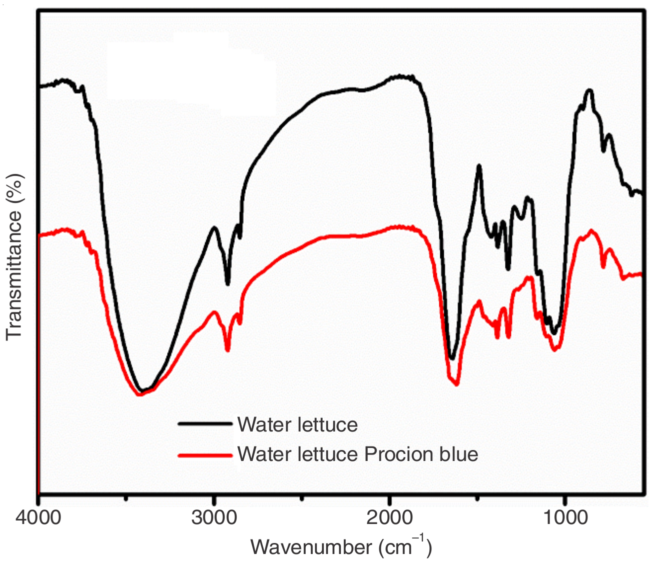

Fig. 2. FT-IR of water lettuce before and after adsorption of procion blue

–OH deformation. The peak at 778 cm^{-1} is aromatic compounds. The intensities of the peaks increased in the case of procion blue-adsorbed water lettuce [24].

SEM and EDAX analysis: The SEM analysis clearly indicates a honeycomb like morphology with many homogeneous pores with a good possibility for the dye to be adsorbed. Comparison of micrographs of water lettuce sample before (Fig. 3a) and after (Fig. 3b) adsorption shows small dye molecules adsorbed on the surface of the water lettuce biomass. It can be seen from the EDX analysis that the elements present in the biomass both before and after adsorption are carbon, oxygen, sodium, potassium, chlorine and calcium. Oxygen, sodium and calcium increased in weight percentage while carbon, potassium and chlorine decreased in weight percentage in the dye-loaded sample compared to the raw biomass.

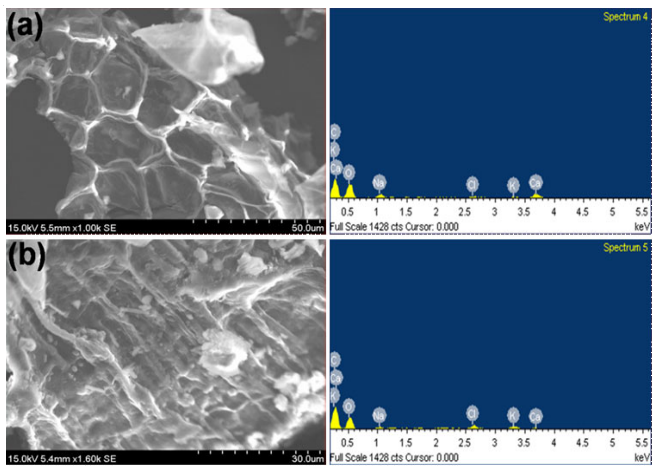

Fig. 3. SEM image and corresponding EDS spectra of water lettuce (a) before adsorption (b) after adsorption

Effect of sorbent dosage: The effect of adsorbent dosage on procion blue dye uptake was investigated by varying the adsorbent dose for water lettuce from 0.1 to 0.5 g at 25 °C. Irrespective of adsorbent dosage, the equilibration time for maximum uptake is found to be 90 min. The equilibrium uptake capacity of procion blue onto water lettuce decreased with increase in dosage of adsorbent (Fig. 4). This is due to the increase in availability of surface active sites resulting from the increased dose and conglomeration of the adsorbent [25].

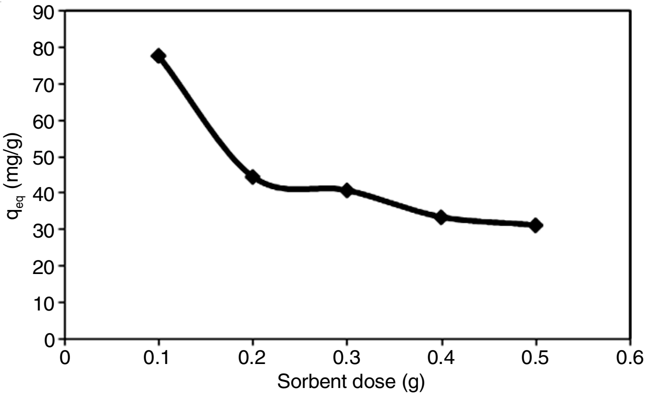

Fig. 4. Effect of biosorbent dosage on biosorption of procion blue using water lettuce (Initial dye conc.: 50 mg/L, Agitation rate: 180 rpm, pH: solution pH)

Effect of pH: pH is an important factor in controlling the adsorption of dye unto the adsorbent. The adsorption of procion blue on water lettuce was studied by varying the pH from 1 to 6, with 0.1g adsorbent dose and 50 mg/L of procion blue dye concentration. The amount of dye adsorbed per unit mass of adsorbent at equilibrium was found to decrease with increasing pH (Fig. 5). This may be due to the protonation of biosorbent material occurring at the lower pH. The protonated biosorbent has more affinity towards the anionic dyes [19].

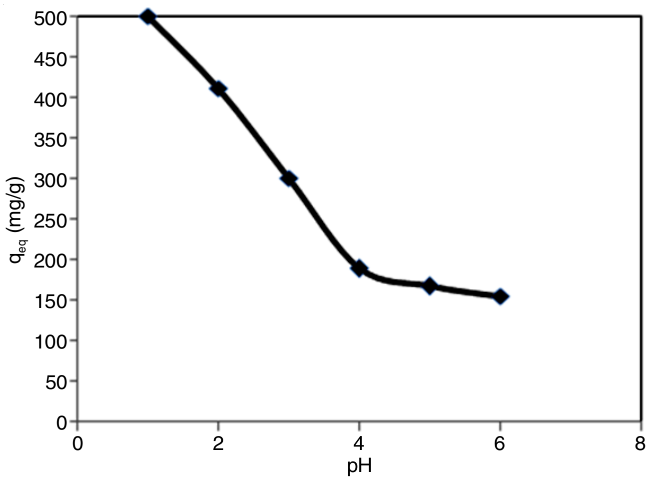

Fig. 5. Effect of pH on biosorption of procion blue using water lettuce (Initial dye conc: 50 mg/L, Agitation rate: 180 rpm, biosorbent dose: 0.1 g)

Effect of initial concentration of dye solution: The initial concentration of procion blue dye solution varied from 25 to 200 mg/L and batch experiments were carried out with 0.1 g adsorbent dose and pH = 1 at 25 °C. The dye uptake capacity increases, as the concentration of the dye solution and time increases. There is initial rapid decrease in concentration of procion blue for about 15 min (Fig. 6) and as it reached equilibrium there was no change in adsorption. This may be due to the formation of concentration gradient between the solid and liquid phase, which might serve as a driving force for the maximum uptake of dye by the biosorbent [26].

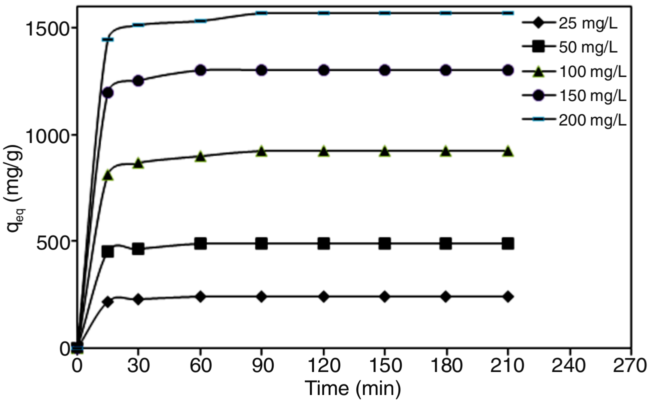

Fig. 6. Effect of initial dye concentration on the uptake capacity of procion blue using water lettuce at different time intervals (Biosorbent dosage: 0.1 g, pH: 1, Agitation rate: 180 rpm)

Adsorption isotherm: Adsorption isotherms represent the equilibrium distribution of dye molecules between the aqueous and solid phases, when the dye concentration increases. The binding of the procion blue dye onto water lettuce was then considered in terms of the Langmuir and Freundlich isotherm equations; the following linearized forms being used:

$$\text{For Langmuir: } \frac{C_{eq}}{q_{eq}} = \frac{C_{eq}}{Q°} + \frac{1}{bQ°} \tag{2}$$

where, q_{eq} (mg/g) and C_{eq} (mg/L) are the amount of dye biosorbed per unit weight of biomass and unbiosorbed dye concentration in solution at equilibrium, respectively. Q° is the maximum amount of dye biosorbed per unit weight of biomass required to form a complete monolayer on the surface and b is a constant related to the affinity of the binding sites (L/mg) [27].

$$\text{For Freundlich: } \ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{3}$$

where, q_{eq} (mg/g) and C_{eq} (mg/L) are the amount of dye biosorbed per unit weight of biomass and unbiosorbed dye concentration in solution at equilibrium, respectively. K_F is the biosorption capacity and n is the biosorption intensity.

The adsorption follows the Langmuir equation; a plot of C_{eq}/q_{eq} *versus* C_{eq} shows a straight line (Fig. 7). Q° can be determined from the intercept and slope. The isotherm was found to be linear over the entire range of concentration studied with a good correlation coefficient R^2 of 0.9970. The value of the correlation coefficient is higher than the Freundlich isotherm value. The fact that Langmuir isotherm fits the experimental data better validates the monolayer coverage of dye on water lettuce and homogeneous distribution of active sites on the adsorbent, since Langmuir adsorption assumes the adsorbent surface to be homogeneous. The equilibrium data was also analyzed according to the linear form of Freundlich isotherm given by equation 3. A plot of ln q_{eq} *versus* ln C_{eq} is shown in Fig. 8 from which K_F and n can be computed and is shown in Table-1. The value of correlation coefficient is much lower (R^2 = 0.9654) than Langmuir isotherm values. This shows that Freundlich isotherm is a poorer fit of experimental data compared to Langmuir isotherm.

Adsorption kinetics: The chemical kinetics of adsorption helps calculate reaction rates and describes reaction pathways whereas chemical equilibrium gives no information about reaction paths. The adsorption kinetic data of procion blue are analyzed using two kinetics models, pseudo-first-order and pseudo-second-order models. The best model is selected based on the linear regression correlation coefficient, R^2 values.

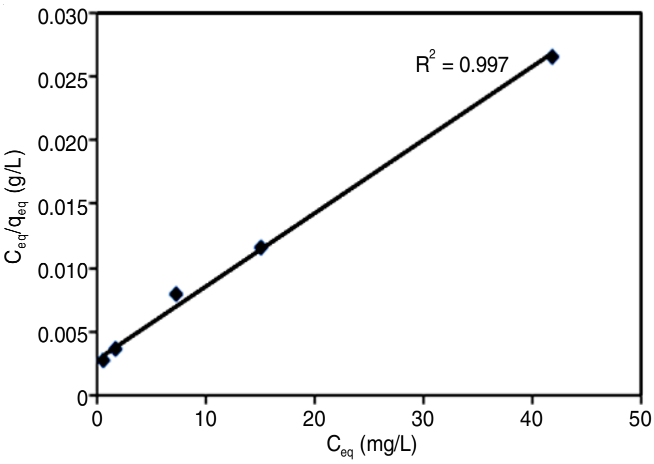

Fig. 7. Langmuir adsorption isotherm model for the biosorption of procion blue dye using water lettuce (Biosorbent dosage: 0.1 g, pH: 1, Agitation rate: 180 rpm)

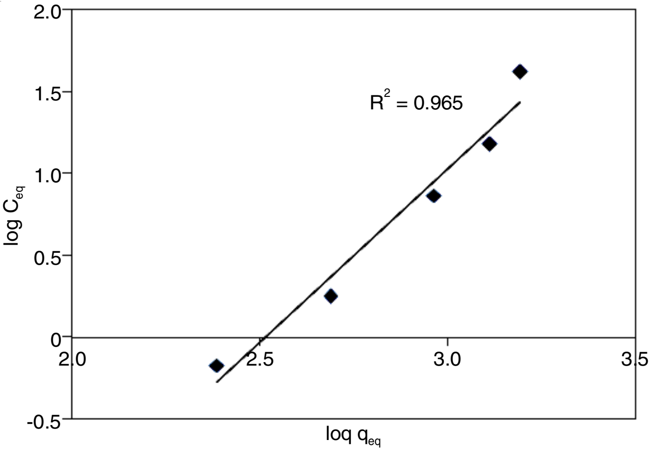

Fig. 8. Freundlich adsorption isotherm model for the biosorption of procion blue dye using water lettuce (Biosorbent dosage: 0.1 g, pH: 1, Agitation rate: 180 rpm)

TABLE-1
ADSORPTION ISOTHERM PARAMETERS FOR PROCION BLUE ADSORPTION ONTO WATER LETTUCE DEAD BIOMASS

Langmuir constants			Freundlich constants		
Q° (mg/g)	b (L/mg)	R^2	K_F	n	R^2
769.23	0.0004	0.997	212.724	0.469	0.9654

Pseudo-first order model: The Pseudo-first order model was proposed by Lagergren [28] in 1898 for adsorption of solutes from a liquid. The pseudo-first order rate equation is

$$\frac{dq}{dt} = k_1(q_e - q_t) \tag{4}$$

The integrated form of eqn. 4 is

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{5}$$

where q_t (mg/g) and q_{eq} (mg/g) are milligrams of dye adsorbed per gram of adsorbent at a given time and equilibrium respectively and k_1 is the rate constant (min^{-1}) of first order adsorption. The plot of log ($q_{eq} - q_t$) against t, gives a straight line as shown in Fig. 9, k_1 and q_{eq} can be determined from the slope and intercept of the plot respectively. It is presented in Table-2. The correlation coefficients for the first-order kinetic model are relatively low and the calculated q_{eq} were not comparable with the experimental q_{eq}. It was also observed that the Lagergren model fits the experimental data only for the first 30 min after which it was found to deviate. Thus, it is observed that the adsorption process does not follow the Lagergren model.

Pseudo-second order model: The pseudo-second order model [29-31] based on the assumption that the adsorption capacity is proportional to the number of active sites occupied on the adsorbent can be written as follows:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{6}$$

The integrated form of eqn. 6 is

TABLE-2
KINETIC PARAMETER FOR THE ADSORPTION OF PROCION BLUE BY WATER LETTUCE DEAD BIOMASS

C_0 (mg/L)	q_{eq}, exp (mg/g)	Pseudo-first order model			Pseudo-second order model		
		k_1 (min^{-1})	q_{eq}, cal (mg/g)	R^2	k_2 (g/mg min)	q_{eq}, cal (mg/g)	R^2
25	244.44	0.0205	24.04	0.5932	0.0052	243.90	0.9990
50	488.89	0.0237	39.72	0.6054	0.0030	500.00	1.0000
100	922.22	0.0311	151.11	0.7740	0.0008	909.09	0.9990
150	1300.00	0.0288	87.04	0.6214	0.0012	1428.57	0.9999
200	1566.67	0.0327	197.33	0.7643	0.0007	1562.50	1.0000

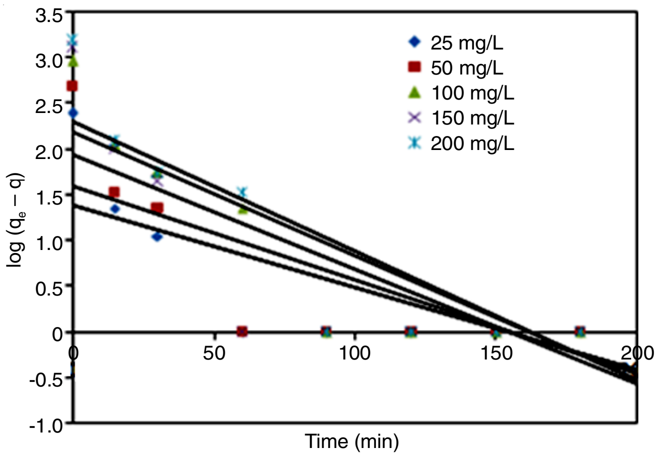

Fig. 9. Pseudo-first order plot for the biosorption of Procion blue using water lettuce biomass

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} - \frac{1}{q_e} t \qquad (7)$$

where q_t (mg/g) and q_{eq} (mg/g) are milligrams of dye adsorbed per gram of adsorbent at a given time (t) and equilibrium respectively and k_2 is the rate constant (min^{-1}) of second order adsorption. The plot of t/q_t against t, gives straight line as shown in Fig. 10, k_2 and q_{eq} can be determined from the slope and intercept of the plot. The correlation coefficients R^2 were found to be between 0.999-1. The theoretical q_{eq} values were also very close to the experimental q_{eq} values in the-second order model. It is clear from the good fit of this model that the adsorption kinetics of procion blue is best described by second order chemical reaction and that this reaction is vital in the rate-determining step. Pseudo-second order kinetic model suggests that the adsorption of procion blue on water lettuce is involved with the sorption on the external surface and diffusion into the interior of adsorbent.

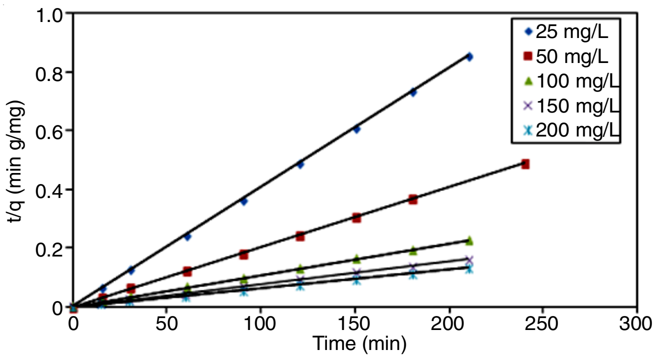

Fig. 10. Pseudo-second order plot for the biosorption of procion blue using water lettuce biomass

A comparison of calculated and experimental equilibrium uptake of procion blue dye is shown in Fig. 11. The pseudo-second order equation provides the best correlation of the adsorption process at all initial concentrations. The pseudo-first order equation does not give a good fit to the experimental data for the adsorption of procion blue.

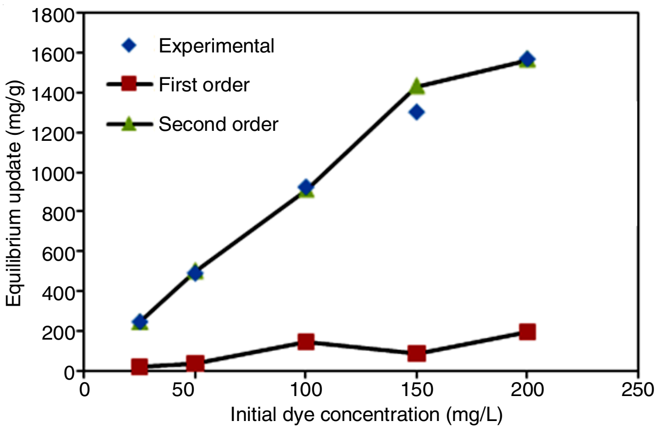

Fig. 11. The calculated and experimental equilibrium dye uptake values for the biosorption of procion blue at different initial dye concentrations using water lettuce based on first- and second-order kinetic models

Conclusion

The present investigation shows that water lettuce (*Pistia stratiotes*) can be used as a potential adsorbent for the removal of procion Blue H-5R from aqueous solutions over a wide range of concentration. Batch adsorption studies reported a maximum equilibrium dye adsorption capacity of 1566.67 mg/g at optimum pH of 1, contact time 90 min, adsorbent dose of 0.1 g and initial dye concentration of 200 ppm. Adsorption behaviour of procion blue onto water lettuce is described by a mono layer Langmuir type isotherm and the kinetic data obtained best fits the pseudo-second order kinetic model. SEM analysis reveals that the porous honeycomb-like structure of sorbent highly favours dye adsorption. It may be concluded that the water lettuce may be used as a natural, economical and easily available sorbent for effective removal of procion blue from aqueous solutions.

REFERENCES

1. T. Robinson, G. Mcmullan, R. Marchant and P. Nigam, *Bioresour. Technol.*, **77**, 247 (2001).
2. G. Mishra and M.A. Tripathy, *Colourage*, **40**, 35 (1993).
3. I.M. Banat, P. Nigam, D. Singh and R. Marchant, *Bioresour. Technol.*, **58**, 217 (1996).
4. Y. Fu and T. Viraraghavan, *Bioresour. Technol.*, **79**, 251 (2001).
5. E. Clarke and R. Anliker, Organic Dyes and Pigments, In: The Handbook of Environmental Chemistry, vol. 3, pp. 181-215 (1980).

6. A.K. Mittal and S. Gupta, *Water Sci. Technol.*, **34**, 81 (1996).
7. H. Chu and K. Chen, *Process Biochem.*, **37**, 595 (2002).
8. W.Z. Tang and H. An, *Chemosphere*, **31**, 4171 (1995).
9. I. Koyuncu and H. Afsar, *J. Environ. Sci. Health A*, **31**, 1035 (1996).
10. R.J. Davis, J.L. Gainer, G. O'Neal and I.W. Wu, *Water Environ. Res.*, **66**, 50 (1994).
11. P. Cooper, *J. Soc. Dyers Colour.*, **109**, 97 (1993).
12. P.C. Vandevivere, R. Bianchi and W. Verstraete, *J. Chem. Technol. Biotechnol.*, **72**, 289 (1998).
13. B. Nandi, A. Goswami and M. Purkait, *Appl. Clay Sci.*, **42**, 583 (2009).
14. S. Chowdhury, S. Chakraborty and P. Saha, *Colloids Surf. B*, **84**, 520 (2011).
15. S. Dawood and T.K. Sen, *Water Res.*, **46**, 1933 (2012).
16. S. Ibrahim, I. Fatimah, H.-M. Ang and S. Wang, *Water Sci. Technol.*, **62**, 1177 (2010).
17. K.S. Low, C.K. Lee and K.K. Tan, *Bioresour. Technol.*, **52**, 79 (1995).
18. V. Karthik, M. Velan, M.D. Kumar and S. Renganathan, *Can. J. Chem. Eng.*, **87**, 554 (2009).
19. S. Renganathan and P. Gautam, *Chem. Prod. Process Model*, **3**, 1 (2008).
20. N. Praveena, P. Saravanan, M. Dharmendira Kumar, N. Nagendra Gandhi and S. Renganathan, *Asia-Pac. J. Chem. Eng.*, **7**, 761 (2012).
21. N. Naveen, P. Saravanan, G. Baskar and S. Renganathan, *J. Taiwan Inst. Chem. Eng.*, **42**, 463 (2011).
22. http://www.dcnr.state.pa.us/cs/groups/public/documents/document/dcnr_010308.pdf.
23. P. Miretzky, A. Saralegui and A.F. Cirelli, *Chemosphere*, **57**, 997 (2004).
24. L.K.S. Lima, J.F.L. Silva, M.G.C. da Silva and M.G.A. Vieira, *Chem. Eng. Transac.*, **38**, 97 (2014).
25. G.M. Ratnamala and K. Brajesh, *Int. J. Environ. Sci. Technol.*, **2**, 80 (2013).
26. S. Renganathan, J. Kalpana, M. Dharmendirakumar and M. Velan, *Clean-Soil Air Water*, **37**, 901 (2009).
27. K.S. Low and C.K. Lee, *Bioresour. Technol.*, **61**, 121 (1997).
28. S. Lagergren, *K. Sven. Vetensk. Akad. Handl.*, **24**, 1 (1898).
29. Y.S. Ho and G. Mckay, *Process Biochem.*, **34**, 451 (1999).
30. Y.S. Ho and G. Mckay, *Chem. Eng. J.*, **70**, 115 (1998).
31. Y.S. Ho and G. Mckay, *Water Res.*, **34**, 735 (2000).