

Investigation of a Basic Dye Adsorption Characteristics of a Non-Living Submerged Aquatic Plant (*Myriophyllum spicatum*)

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In this paper, the adsorption properties of *Myriophyllum spicatum* (Eurasian watermilfoil) for a basic dye (basic blue 41) were investigated as a biosorbent and the results were compared with other biosorbents. Data obtained from the initial batch adsorption studies have indicated that dried *M. spicatum* is capable of removing basic blue 41 from the solution. The dye biosorption was fast and equilibrium was attained within 20 min. Data obtained from further batch studies applied to Langmuir and Freundlich Models. High correlation coefficient with Linearized Langmuir Model was observed, however, negative q_{\max} value was observed indicating the inadequacy of Langmuir model. High correlation coefficient was also obtained with application of linearised form Freundlich model and it was found more suitable for the dye plant system. The kinetics of adsorption of basic blue were also analyzed and rate constants were derived for various dye concentrations. Initial part of the adsorption was found to be governed by film diffusion process. It was also found that the overall adsorption process was best described by the pseudo second order kinetics. Gibbs free energy value was found to be -2.2793 kJ and indicating the spontaneity of the system. The results showed that this submerged aquatic plant *M. spicatum* can be successfully used for the removal of basic blue 41.

Key Words: Aquatic plants, Biosorption, Basic dye, Freundlich model, Pseudo second order.

INTRODUCTION

Textile industries are one of the leading industries in many part of the world that uses significant amount of chemicals in order to obtain high quality products. Dyes are one of those chemicals that became the subject of many research in past years because of the potentially adverse impact on the environment. Dyes are used in various industries including food and pharmaceutical industries, but those used in textile industry are particularly less biodegradable than many other carbonaceous wastes because of their structures are designed to resist all kind of environmental conditions.

Because of the low biodegradability and potential of harmful effects to the environment, dyes are subject to many different treatment technologies. Adsorption is one of the techniques which have been used for long time for the removal of various pollutants from both potable water and wastewater and activated carbon is the most widely used as adsorbent. There have been significant research on biosorbents for the removal of organic pollutants particularly dyes from the wastewater¹.

Aquatic plants are such examples to those biosorbents and it has been long known that aquatic plants, both living and dead, are heavy metal accumulators. Therefore, the use of aquatic plants for the removal of heavy metals from wastewater gained more interest²⁻⁴. Some freshwater macrophytes including *Potamogeton lucens*, *Salvinia herzogoi*, *Eichhornia crassipes*, *Myriophyllum brasillensis*, *M. spicatum*, *Cabomba* sp., *Ceratophyllum demersum* have recently been investigated for the removal of heavy metals⁵⁻⁷. However for the dye removal limited amount of works were published so far. Low *et al.*⁸ studied the removal of methylene blue and basic blue by *Hydrilla verticillata* under different experimental conditions. They reported that dried *H. verticillata* removed both basic dyes efficiently.

In another work of Low *et al.*⁹ on the potential of the biomass of non-living, dried, roots of water hyacinth (*Eichhornia crassipes*) to remove two basic dyes, methylene blue and victoria blue from aqueous solutions. Various parameters was also studied including pH, sorbent dosage, contact time and initial concentrations. They reported that the Langmuir isotherm was found to represent the measured sorption data well. Lee *et al.*¹⁰ has studied the potential of the biomass of non-living water hyacinth (*E. crassipes*) roots as a biosorbent for anionic dyes. Various parameters affecting the sorption of acid blue 25 and reactive blue 2 on water hyacinth roots were studied. They investigated the effect of pH, initial dye concentration, temperature, agitation rate and sorbent concentration. Sorption was found to increase as pH decreased and temperature increased. According to their kinetic studies, boundary layer and intraparticle diffusion played important roles in the rate of dye removal. Waranusantigul *et al.*¹¹ have studied biosorption of methylene blue by giant duckweed (*Spirodela polyrrhiza*). They investigated system variables like sorbent dosage, pH, contact time and reported that sorption at pH values between 3 and 11 was remarkable. Zawary and Kamel¹² have recently studied the removal of azo and anthraquinone dyes from aqueous solutions by *E. crassipes* as an biosorbents. According to their work data fit well to the Freundlich model.

Some submerged aquatic plants are invasive and can be seen generally in aquatic environments like streams, littoral zones of the lakes, drainage systems and wetlands. In Cukurova, the agricultural areas are very large

and drainage channel systems are common around the fields for irrigation. *M. spicatum* is very common in these drainage systems and can be found throughout the year.

M. spicatum (Eurasian watermilfoil) is a submerged aquatic perennial plant which reproduces primarily by vegetative fragmentation. These fragments are produced during much of the year with the roots often developing on a fragment before it is released by the plant¹³. Plants may grow in water from 0.5 to 10 m deep. However, most plants appear to grow in water 0.5 to 3.5 m deep. It is rooted to the bottom and grows to the surface. Flowering and seed production are common. However, the seeds exhibit prolonged dormancy and their germination is erratic¹⁴.

The main purpose of this study, therefore, is to investigate the adsorption characteristics of basic blue 41 onto water milfoil (*M. spicatum*).

EXPERIMENTAL

The plant biomass, which had been harvested locally, was washed with diluted HCl solution (3%) and distilled water. Afterwards, they were dried at 90°C for 24 h and broken into small pieces, sieved and the particles with a diameter 0.42 mm was used. The dye was obtained from a local textile mill. The sorption tests were conducted at 25°C in conical flasks (250 mL) using an orbital shaker in a constant room temperature. *M. spicatum* biomass (ca. 2 g) was added to each flask and placed on the orbital shaker. The initial dye concentrations for the contact time experiments was 25, 50, 100, 200 and 400 mg/L and the incubation times ranged from 5 to 160 min. The data used to derive the Langmuir and Freundlich constants were obtained by using *M. spicatum* biomass (2 g) and dye concentrations of 25, 50, 100, 200 and 400 mg/L. The contact time was 1 h. After contacting, the contents of the flask were filtered to separate the biomass from the solution. Residual dye concentrations were measured spectrophotometrically (Bausch and Lomb, Spectronic 21) as the absorbance at 609 nm for basic blue 41, which was the wavelength giving maximum absorbance. The results of dye analysis were used to calculate specific adsorption (mg dye adsorbed/g of biomass, dry weight). The amount of dyes adsorbed by *Myriophyllum spicatum* biomass was calculated using the following equation:

$$q=V(C_i-C_e)/W$$

where q (mg/g) is the amount of dye sorbed by activated sludge, C_i and C_e (mg/L) are initial and equilibrium dye concentration in liquid phase, V is the volume of solution (L) and W is the dry weight of *M. spicatum* biomass (g).

All the experiments were duplicated and results quoted as mean values. The variation of the actual results from the mean values was < 5%.

RESULTS AND DISCUSSION

Basic adsorption

Initial adsorption tests showed that *M. spicatum* adsorbed basic blue 41 (Fig. 1). The data also showed that significant adsorption occurs in just 20 min; however 1 h was chosen to achieve to equilibrium. After these initial experiments, further adsorption tests were carried out.

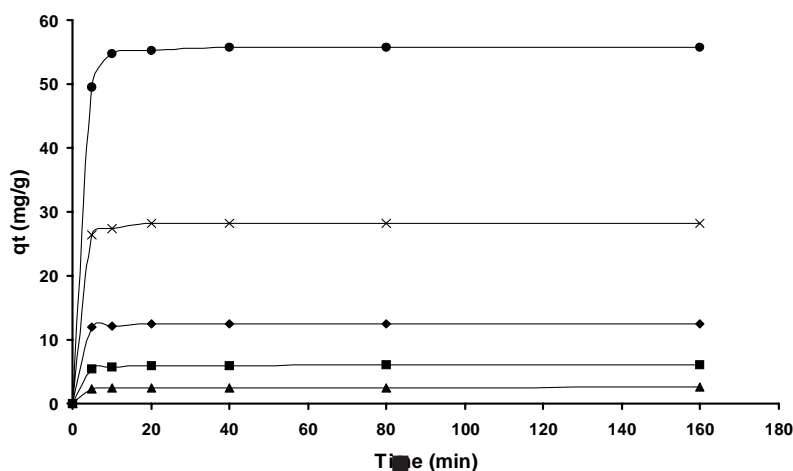


Fig. 1. Variation of specific adsorption with time for various initial dye concentration for various dye concentrations (25 mg/L ▲, 50 mg/L □, 100 mg/L ◆, 200 mg/L × and 400 mg/L ●)

The linearized form of the Langmuir equation can be written as:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \left(\frac{a_L}{K_L} \right) C_e$$

where; C_e = the equilibrium concentration of adsorbate in solution after adsorption (mg/L), q_e = the equilibrium solid phase concentration (mg/g), K_L (L/g) and a_L (L/mg) = the Langmuir constants.

The linearized form of the Freundlich model can be written as:

$$\log(q_e) = \log(K_f) + \frac{1}{n} \log(C_e)$$

where; C_e = the equilibrium concentration of adsorbate in solution after adsorption (mg/L), q_e = the equilibrium solid phase concentration (mg/g), K_f (L/g) and Freundlich constants (n) related with adsorption capacity and intensity. The initial batch sorption experiments showed that equilibrium had been achieved with in 1 h (Fig. 1). Therefore, this was used as the contact time for the subsequent work which derived values of Langmuir and Freundlich constants. Regression equations were found $y = -0.2549x + 9.0592$ for Langmuir model and $y = 2.2682x - 2.108$ for Freundlich model.

Constants were derived from these equations are shown in Table-1 along with various dye-biosorbent systems. As can be seen from Table-1, although better correlation coefficient was obtained from Langmuir model, however value of q_{\max} was found negative. This negative value was also reported by Robinson *et al.*¹⁵ which indicate that Langmuir model was not sufficient to describe this dye plant sorption system. The application of Freundlich model yielded high correlation coefficient for dye *M. spicatum* system, however low K_f value was obtained. It was already reported that for the favourable adsorption 'n' must be higher than unity. Similar results were also reported by Namasivayam *et al.*¹⁶ for rhodamine-B and coir pith system. A comparison of regression results with this current study along with various dye-biosorbent systems are shown in Table-1.

TABLE-1
COMPARISON OF LANGMUIR AND FREUNDLICH CONSTANTS
FOR VARIOUS DYE-SORBENT SYSTEMS

Adsorbent	Dye	Langmuir constants				Freundlich constants		
		q_{\max} (mg/g)	a_L (L/mg)	K_L (L/g)	R^*	K_f (L/g)	n	R^*
<i>M. Spicatum</i> (This work)	Basic blue 41	-3.928	-0.028	0.110	0.964	0.0078	0.440	0.954
Coir pith ¹⁶	Rhodamine-B	2.560	2.743		0.995	0.0240	0.732	0.894
Water hyacinth roots ¹⁰	Acid Blue 25	107.5						
Water hyacinth roots ¹⁰	Reactive Blue 2	58.8						
Water hyacinth roots ⁹	Methylene Blue	128.9						
Water hyacinth roots ⁹	Victoria Blue	145.4						
Wheat straw ¹⁵	Dye mixtures	-3.78	0.360	-1.3608		-4.1000	3.420	

*R = correlation coefficient.

Kinetics of adsorption

The adsorption process in porous solids can be separated into three stages. First stage is diffusion through the solution to the external surface of the adsorbent and also called film mass transfer or boundary layer diffusion of solute molecules. Second stage is diffusion within the pores or capillaries of the adsorbent internal structure to the sorption sites while in third steps rapid uptake occurs^{17,18}. However, the third step is immeasurable fast and therefore contributes no resistance to the adsorption process; so film mass transfer and intraparticle diffusion remain the rate determining steps¹⁹. Therefore, film transfer controls for the initial part adsorption for the first few min of the process and is not rate controlling process.

Intraparticle diffusion on the other hand, occurs over longer time and constituting the main course of adsorption¹⁹.

External mass transfer or boundary layer diffusion can be characterized by the initial rate of solute sorption. It was already demonstrated that the initial part of the adsorption of various basic dyes by some biological materials is controlled by film diffusion and fit to the first order process according to the following equation^{20,21}:

$$-kt = 2.303 \log \frac{C_t}{C_0}$$

where C_t is concentration of dye remaining at the each contact time t , C_0 is initial dye concentration of dyestuff and k is the reaction rate constant.

Initial rate can be calculated from the initial slope of the $-\log C_t/C_0$ and time curves (Fig. 2). These slopes can be derived by assuming that relationship was linear for first 5-10 min²¹⁻²³. Initial rates calculated on this basis are given in Table-2. High correlation coefficients were obtained for the basic blue 41 and *M. spicatum* system and initial rates increased with increasing dye concentrations. This indicates that initial part of the adsorption process governed by first order boundary layer diffusion. This finding is in consistent with earlier reports^{20,21}.

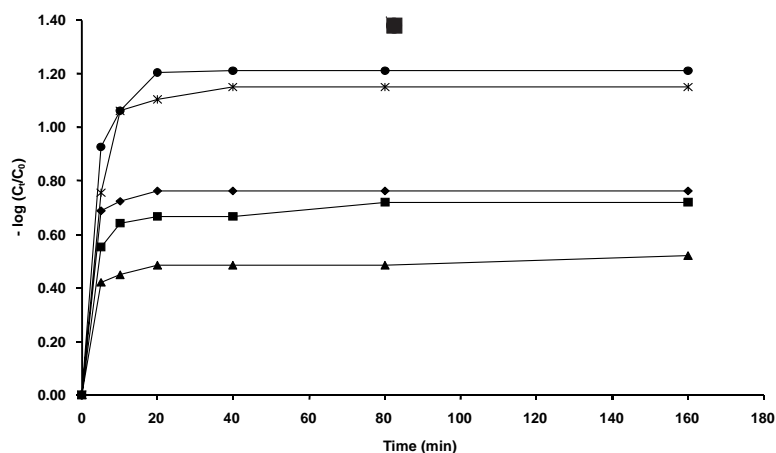


Fig. 2. Variation of $-\log C_t/C_0$ with contact time for basic blue 41 (25 mg/L ▲, 50 mg/L ◻, 100 mg/L ◆, 200 mg/L × and 400 mg/L ●)

In many cases, there is the possibility that intraparticle diffusion will be the rate limiting step and this normally determined by using the equation described by Weber and Morris²⁴:

$$k_p = \frac{q}{t^{1/2}}$$

where; q (mg/g) is the amount of the metal adsorbed at time t , k_p is the intraparticle rate constant (mg/g min^{0.5}).

TABLE-2
INITIAL RATE CONSTANTS CALCULATED FROM $-\log C_T/C_0$ vs.
CONTACT TIME FOR BASIC BLUE 41 AND *M. SPICATUM*

Initial dye concentration (mg/L)	k (per min)	R
25	0.045	0.895
50	0.064	0.923
100	0.072	0.887
200	0.106	0.919
400	0.107	0.972

Fig. 3 shows that the relationships for the *M. spicatum* and basic blue 41 system are not linear over the entire time range, indicating that more than one process is affecting the adsorption. This type of non-linearity has been reported previously by various authors and has been interpreted as showing that both boundary layer diffusion, the initial curved portion and intraparticle diffusion, the final linear portion, are occurring^{18,25-28}. The slope of final linear portion can be used to derive a rate parameter (k_p) for intraparticle diffusion. It is also possible to derive an initial rate parameter (j) by linear regression between $t = 0$ and t_{im} which is the first breakpoint in the relationship¹⁸. Values for these parameters are given in Table-3.

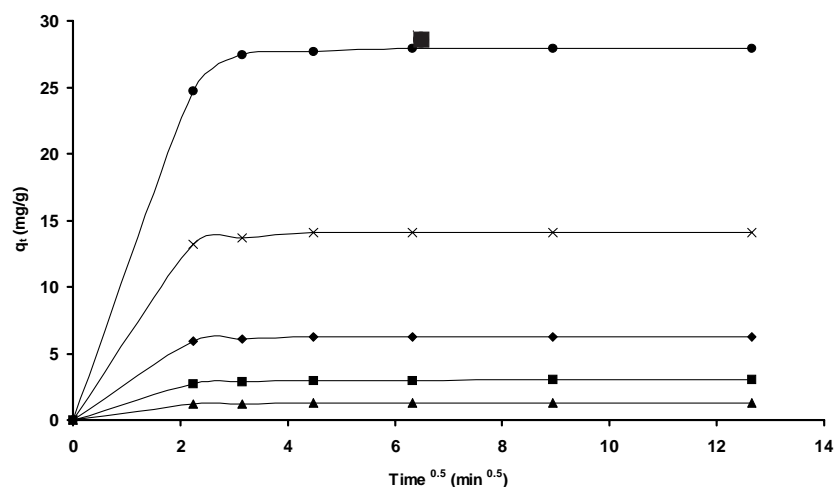


Fig. 3. Plots for the intraparticle diffusion for basic blue 41 *M. spicatum*
(25 mg/L ▲, 50 mg/L ■, 100 mg/L ◆, 200 mg/L × and 400 mg/L ●)

For the kinetics of adsorption, first order Lagergren expression, second order and pseudo second order models were all examined. In all three models, it was found that the pseudo second order approach provided excellent results.

The pseudo second order equation¹⁸ is:

$$t/q_t = [1/Kq_e^2] + t/q_e$$

where q_e is the mass of metal adsorbed at equilibrium (mg/g), q_t is the mass of metal at time t (min), K is the pseudo second order rate constant of adsorption ($\text{g mg}^{-1} \text{min}^{-1}$).

TABLE-3
INTRAPARTICLE RATE CONSTANTS FOR BASIC BLUE 41 AND
M. SPICATUM FOR VARIOUS INITIAL DYE CONCENTRATIONS

Initial dye concentration (mg/L)	Initial rate constants (j) ($\text{mg/g min}^{0.5}$)	R	k_p ($\text{mg/g min}^{0.5}$)	R
25	0.407	0.968	0.0080	0.883
50	0.968	0.974	0.0158	0.921
100	2.595	0.963	0.0084	0.583
200	4.029	0.967	0.0265	0.600
400	9.107	0.979	0.0446	0.778

The plot of the t/q_t vs. t for various dye concentrations are shown in Fig. 4 and values of the reaction rate constants and correlation coefficients for each dye concentrations are listed in Table-4.

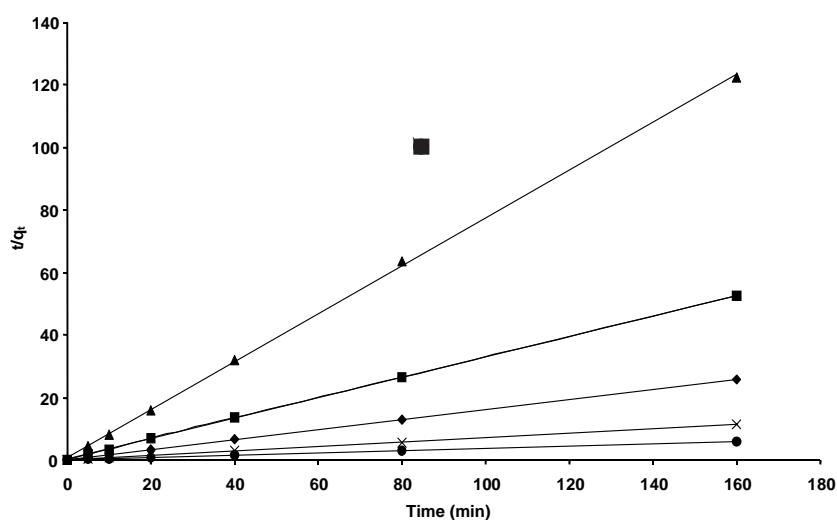


Fig. 4. Pseudo second order rate plot (25 mg/L ▲, 50 mg/L ■, 100 mg/L ◆, 200 mg/L × and 400 mg/L ○)

TABLE-4
PSEUDO SECOND ORDER RATE CONSTANTS FOR BASIC BLUE 41
AND *M. SPICATUM* FOR VARIOUS INITIAL DYE CONCENTRATIONS

Initial dye concentration (mg/L)	K (mg/g min)	R
25	0.8415	0.999
50	0.5515	0.999
100	1.7557	1.000
200	0.5041	1.000
400	0.1602	1.000

Thermodynamics of adsorption

It is well known fact that Gibbs free energy would define system spontaneity. Gibbs free energy (ΔG°) can be calculated from the followings²⁹:

$$K_c' = C_a / C_e$$

$$\Delta G^\circ = -RT \ln K_c^\circ$$

where K_c is the equilibrium constant, K_c° is the thermodynamic equilibrium constant C_a is the solid phase concentration in equilibrium (mg/L), C_e is the equilibrium concentration in solution (mg/L), R is the universal gas constant (J/mol K) and T is temperature (K). Thermodynamic equilibrium constant (K_c°) can be calculated from the equilibrium constant by plotting equilibrium constant against initial dye concentration^{30,31}. Value of Gibbs free energy calculated on this basis is -2.279 kJ/mol. This negative value of the Gibbs free energy indicates the spontaneity of the sorption of basic blue 41 on to *M. spicatum*. Table-5 shows the comparison of Gibbs free energy values for various adsorbents.

TABLE-5
COMPARISON OF GIBBS FREE ENERGY VALUES FOR
VARIOUS SYSTEMS

Sorbent	Dye	ΔG° (kJ/mol)	T (K)
<i>M. spicatum</i> (This work)	Basic blue 41	-2.279	298
Activated carbon ³²	Methyl violet	-3.200	289
Neem leaf powder ³³	Brilliant green	-7.150	300
Fuller's earth ³⁴	Methylene blue	-27.340	298
Tree fern ³⁵	Basic red 13	-9.590	293

Conclusions

From the work presented here, following conclusion can be drawn: (i) *Myriophyllum spicatum* can be effective as a biosorbent for the removal basic blue 41, (ii) data obtained from equilibrium studies fit both Langmuir and Freundlich models however for the Langmuir model negative q_{\max} value was obtained and indicating the inadequacy of this model for this particular dye-plant system, (iii) initial part of the adsorption governed by first degree film diffusion process and also intraparticle diffusion is significant, (iv) overall adsorption process was best described by pseudo second order model and (v) Gibbs free energy value was also calculated and -2.279 KJ/mol was found, indicating the spontaneity of adsorption process.

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