CHAPTER 5
Adsorption of an anionic dye, Erythrosine B on PSLW carbon

5.1 Introduction

The textile industry is one of the main exchequers of many countries. This economic activity generates coloured waste water depending on the degree of fixation of dyes onto the substrates and this varies with the nature of substances, intensity of dyeing and the application method [1-3]. The effluents containing dyes and pigments cause environmental problems and they are of serious concern in recent years [4]. Some of the dyes are very toxic and display carcinogenic and mutagenic effects on aquatic biota and human being [5]. Colour restricts penetration of solar radiations and retards photosynthesis which results in increase of COD and BOD levels of aquatic sources. Erythrosine B is a popular dye that has been widely used in cosmetics, foodstuffs, medicines and textiles. It is highly toxic to mankind and it may lead to many diseases including carcinogenicity.

Important methods available for the removal of dyes and pigments from waste water include physical adsorption, chemical degradation, biological degradation, photo degradation, ion exchange method and reverse osmosis [6]. Most of the above methods have one or another limitation and none of them was successful at economic level [7,8]. Among other techniques, adsorption still exhibits advantages because of its treatment efficiency, absence of any by-products, inexpensiveness and swiftness in nature. Activated carbon is a well-known material for dye adsorption but its application is restricted owing to its high production cost, as it is prepared from non-renewable sorption material such as coal. This has resulted in a growing interest in search of the production of activated carbon from cheaper renewable precursors like agricultural by products [9] in recent years. Recently a number of low cost, easily available biological
materials such as carrot stem and leaf powder [10], milled sugarcane [11], *Achyranthes aspera* leaf powder [12], *Strychnos potatorum* seeds [13], parsley stalks [14], banana peels [15], rice bran [16], sugarcane bagasse [17] etc., have been used as potential alternative adsorbents for the removal of dyes from effluents.

In the present work, removal of Erythrosine B (ErB) dye from aqueous solution is attempted with carbon prepared from a plant material, *Prosopis spicigera* L. wood (PSLW), which is available all over India especially in the dry lands and deserts and is used as firewood. The PSLW carbon is cheap, cost effective and widely available but its adsorption behaviour, in particular towards dyes is not much studied. Hence in the present work, an anionic dye ErB is chosen, which is photo stable and not easily degradable to investigate its adsorption on PSLW carbon. With many active sites and pores, the PSLW carbon is expected to have efficient adsorbent. The results presented herein not only confirm this point but also display the interesting and typical adsorption behaviour of the material.

### 5.2 Batch adsorption studies

#### 5.2.1 Effect of pH

The pH of the solution is an important controlling parameter in the adsorption process and so the role of hydrogen ion concentration is examined covering a range of pH 1.0-10.0. The effect of pH on the sorption of ErB dye is shown in Figure 5.1. The results indicate that the maximum uptake of ErB is found to be at pH 3.0. Hence an optimum pH of 3.0 is chosen for further studies on ErB dye adsorption. This behaviour can be explained on the basis of change in the surface charge of the adsorbent. As the H\(^+\) ion concentration in the aqueous system is high at lower pH, the surface of adsorbent acquires positive charge by adsorbing H\(^+\) ions. The positively charged surface
sites favour the adsorption of anionic dye in a significant way by electrostatic attraction [18].

**Figure 5.1**- Effect of pH on the adsorption of ErB dye on PSLW carbon

When the pH of the aqueous system is higher than 7.0, negatively charged sites on the surface increase as the result of adsorption of OH\(^{-}\) ions. The negatively charged surface sites do not favour the adsorption of anionic dye due to the electrostatic repulsion which causes decrease in the adsorption. Similar results are reported for the adsorption of anionic dye, Orange G on unmodified sheesham (*Dalbergia sisso*) saw dust from aqueous solution [19].

This conclusion emerges from the observation of desorption and IR study. With ethanol and chloroform, minimum dye desorption (26.8 and 7.8 % respectively) takes place while with sodium hydroxide, maximum dye desorption (38.56 %) is observed. Desorption study with sodium hydroxide clearly suggests the existence of electrostatic interaction while desorption study with ethanol and chloroform suggests the presence of hydrogen bonding and hydrophobic interaction between PSLW carbon and ErB dye during dye adsorption. The adsorption is evident from the IR spectrum of
Figure 5.2-FT-IR spectra of (a) free PSLW carbon and (b) ErB-loaded carbon

Figure 5.3-SEM images of (a) free PSLW carbon and (b) ErB-loaded carbon
ErB-loaded PSLW carbon (Figure 5.2). In the IR spectrum of ErB-loaded PSLW carbon the -C=O stretching frequency of lactone at 1623 cm\(^{-1}\) is shifted to higher wave number side (1631 cm\(^{-1}\)) indicating the presence of electrostatic interaction. Further SEM analysis after adsorption (Figure 5.3b) shows the presence of spherical particles on the surface of ErB-loaded PSLW carbon and this indicates the adsorption of dye molecules on the surface of PSLW carbon.

5.2.2 Effect of contact time and initial dye concentration

Contact time is one of the effective factors in batch adsorption process. The effect of contact time and initial concentration of dye on the extent removal of ErB on PSLW carbon is shown in Figure 5.4. The characteristics of PSLW carbon and its available adsorption sites affect the course of time to reach the equilibrium. The adsorption capacity of ErB dye on PSLW carbon is evaluated at different initial concentrations of ErB dye, 25, 30 and 35 mg/L. The maximum adsorption capacity of ErB dye at three different initial concentrations of 25, 30 and 35 mg/L are found to be 11.38, 13.75 and 15.85 mg/g respectively. Removal of ErB dye by the adsorbent PSLW carbon shows a rapid uptake of ErB dye initially and a gradual/slow uptake at later stage. The removal rate gradually slows down and reaches equilibrium at 60 min. After reaching the state of equilibrium, there is no significant increase in adsorption. Similar behaviour is reported for the adsorption of methylene blue on activated carbon prepared from oil palm empty fruit bunch [20].
5.2.3 Effect of adsorbent dosage

Adsorbent dosage study (Figure 5.5) shows that an increase in adsorbent dose increases the percentage removal of dye. It means that increasing the adsorbent dose, increases the number of adsorption active sites which in turn increases the removal of higher amount of dye [21].

Figure 5.4-Effect of contact time and initial concentration of ErB dye on adsorption

Figure 5.5-Effect of adsorbent dosage on ErB dye adsorption
Also from Figure 5.5, the increase in the adsorbent amount may lead to aggregate the adsorption sites, resulting in decrease in the total available surface area of adsorbent hence the adsorption amount decreases at higher adsorbent amount. Similar results have been reported by McKay et al. [22] on Fuller’s earth and fired clay as adsorbent for dyestuffs.

5.2.4 Effect of adsorption of ErB dye in the presence of other ions

In order to apply this study to industrial applications, batch study was carried out in the presence of mixture of salts, KNO₃, KCl and K₂SO₄ of concentration 0.1 M each. For an initial concentration of 25 mg/L of ErB, the adsorption increases with time and equilibrium is reached at 60 minutes similar to that of free dyes. The adsorption capacity was found to be 12.15 mg/g which is higher than that of adsorption in the absence of salts.

![Graph](image)

**Figure 5.6**-Effect of adsorption of ErB in the presence of KNO₃, KCl and K₂SO₄
5.2.5 Effect of temperature

Temperature plays an important role in determining the adsorption capacity. It was studied by varying the temperature from 30 °C to 45 °C. Figure 5.7 depicts that the adsorption capacity of PSLW carbon decreases with increase in temperature, thereby indicating that the adsorption of ErB dye onto PSLW carbon is an exothermic process [23]. This may be due to the increasing trend to desorb ErB dye from the interface to the solution or the distorted active sites on adsorbent.

![Figure 5.7-Effect of temperature on adsorption of ErB](image)

5.3 Thermodynamic behaviour

The thermodynamic constants such as free energy change ($\Delta G^o$), enthalpy change ($\Delta H^o$) and entropy change ($\Delta S^o$) are the actual indicators to determine the nature of thermodynamic feasibility of the adsorption process. $K$, the equilibrium constant for the adsorption reaction was determined by the method of Khan and Singh [24] by plotting $\ln (q/C_f)$ versus $q$ and extrapolating to zero $q$. The values of thermodynamic parameters are calculated from the variation of the equilibrium constant, $K$ with reciprocal of temperature. The free energy change ($\Delta G^o$), enthalpy change ($\Delta H^o$) and entropy change ($\Delta S^o$) are calculated using equations (5.1 and 5.2).
\[
\ln K = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (5.1)
\]

\[
\Delta G^0 = -RT \ln K \quad (5.2)
\]

A plot of \(\ln K\) versus \(1/T\) is found to be linear. \(\Delta H^0\) and \(\Delta S^0\) are determined from the slope and intercept of the plot and the calculated values are displayed in Table 5.1. The \(\Delta G^0\) values are found to be negative, which indicate that the adsorption process is favourable and spontaneous in nature. The adsorption forces are strong enough to overcome the potential barrier in solid-liquid interface [25]. The negative value of \(\Delta H^0\) indicates that the nature of adsorption process is exothermic and the adsorption is of chemisorption in nature. This is also supported by the decrease in value of uptake capacity of the adsorbent with the increase in temperature (Figure 5.7).

The negative value of \(\Delta S^0\) indicates that the decrease in randomness at the adsorbent-solution interface during adsorption of ErB onto PSLW carbon. Similar results are reported by Mahmoodi et al. [26] on the adsorption of textile dyes on pine cone. Thus from thermodynamic parameters it is concluded that the adsorption process is spontaneous and exothermic in nature [23]. This result is in accordance with the observed values of Langmuir constants, \(Q_o\) and \(b\) which get decreased with increase in temperature.

**Table 5.1**- Thermodynamic parameters for the adsorption of ErB dye on PSLW carbon

<table>
<thead>
<tr>
<th>Temperature (ºC)</th>
<th>-(\Delta G^0) (kJ/mol)</th>
<th>-(\Delta H^0) (kJ/mol)</th>
<th>-(\Delta S^0) (J/mol.K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>9.89</td>
<td></td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>8.87</td>
<td>81.36</td>
<td>236.08</td>
</tr>
<tr>
<td>40</td>
<td>6.81</td>
<td></td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>6.67</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
5.4 Isotherm analysis

Isotherm analysis gives a significant physico-chemical fact for assessing the function of the adsorption process as a complete unit operation. The experimental equilibrium adsorption data were analyzed using Langmuir [27] and Freundlich [28] models. They are used to predict the mechanism of the adsorption and the adsorption capacity of the adsorbent. Langmuir isotherm assumes monolayer coverage of adsorbent and all the sites on the solid surface have equal affinity for adsorbate molecules. It is denoted by equation (5.3) in the linear form,

\[
\frac{C_f}{q} = \frac{1}{Q_0b} + \frac{C_f}{Q_0} \tag{5.3}
\]

where \(Q_0\) and \(b\) are the Langmuir constants indicating the sorption capacity and energy respectively. The Langmuir model, the linear plots of \(C_f/q\) against \(C_f\) for the adsorption of ErB dye on PSLW carbon at different concentrations and temperatures are shown in Figures 5.8 and 5.9 respectively.

![Figure 5.8](image)

**Figure 5.8** - Langmuir isotherm for ErB dye adsorption at different concentrations
The calculated values of $Q_0$ and $b$ at different concentrations and temperatures from the slope and intercept of the linear plots are given in Table 5.2. The values of $Q_0$ and $b$ decrease with temperature and thereby demonstrating favourable adsorption at lower temperature.

The Freundlich isotherm is based on the multilayer adsorption on heterogeneous surface which is defined as below,

$$\log q = \log K_f + \frac{1}{n} \log C_f$$  \hspace{1cm} (5.4)

where $K_f$ and $n$ are Freundlich constants related to the adsorption capacity and adsorption intensity, which can be calculated from the intercept and slope of the linear Freundlich plot of $\log q$ versus $\log C_f$. Though the experimental data fit well to the Langmuir model, they do not fit to Freundlich model. All these facts prove that ErB dye is adsorbed as monolayer coverage on the surface of the adsorbent. Further the dimensionless separation factor ($R_L$) is calculated [29] using equation (5.5):

$$R_L = \frac{1}{1 + bC_0}$$  \hspace{1cm} (5.5)
The observed $R_L$ values lie between zero and one (Table 5.2) which establish the fact that the adsorption process is favourable under the studied conditions. Similar results have been reported earlier for dyes adsorption [30].

Table 5.2-Langmuir isotherm constants at different conditions

<table>
<thead>
<tr>
<th>$C_o$ (mg/L)</th>
<th>Temp. (°C)</th>
<th>$Q_o$ (mg/g)</th>
<th>b (L/mg)</th>
<th>$R_L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>30</td>
<td>9.43</td>
<td>2.42</td>
<td>0.016</td>
</tr>
<tr>
<td>30</td>
<td>30</td>
<td>10.74</td>
<td>1.65</td>
<td>0.021</td>
</tr>
<tr>
<td>35</td>
<td>30</td>
<td>11.99</td>
<td>1.06</td>
<td>0.026</td>
</tr>
<tr>
<td>30</td>
<td>30</td>
<td>10.74</td>
<td>1.65</td>
<td>0.021</td>
</tr>
<tr>
<td>30</td>
<td>35</td>
<td>10.44</td>
<td>1.32</td>
<td>0.025</td>
</tr>
<tr>
<td>30</td>
<td>40</td>
<td>9.97</td>
<td>1.02</td>
<td>0.032</td>
</tr>
<tr>
<td>30</td>
<td>45</td>
<td>9.83</td>
<td>1.01</td>
<td>0.032</td>
</tr>
</tbody>
</table>

5.5 Adsorption kinetics

Adsorption kinetics provides the knowledge on the adsorption mechanism of adsorbate onto an adsorbent. The kinetics of ErB dye adsorption on PSLW carbon has been examined with pseudo-first order [31] and pseudo-second order [32,33] kinetic models.

The pseudo-first order equation is given by Lagergren (equation 5.6),

$$\log(q_e - q) = \log q_e - \frac{k_1}{2.303} t$$

(5.6)

where $q_e$ and $q$ are the amount of dye adsorbed at equilibrium (mg/g) and at time, t and $k_1$ is the adsorption rate constant. The rate constant, $k_1$ is obtained from the plot of log ($q_e - q$) versus t.
The pseudo-second order equation is given below (equation 5.7),

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$  \hspace{1cm} (5.7)

where $q_e$ and $q_t$ are the amount of dye adsorbed (mg/g) at equilibrium and at time, $t$ respectively. $k_2$ is pseudo-second order rate constant for the adsorption which is obtained from the plot of $t/q_t$ versus $t$.

**Figure 5.10**-Pseudo-first order plots at different concentrations of ErB dye

**Figure 5.11**-Pseudo-first order plots at different temperatures of ErB dye
The values of $k_1$ and $k_2$ are obtained from the linear plots of the pseudo-first order (Figures 5.10 and 5.11) and pseudo-second order (Figures 5.12 and 5.13) kinetic models along with the co-efficient of linear correlation ($R^2$) are given in Table 5.3.

**Figure 5.12** - Pseudo-second order plots at different concentrations of ErB dye

**Figure 5.13** - Pseudo-second order plots at different temperature of ErB dye
Table 5.3-Comparison of pseudo-first order and pseudo-second order kinetic parameters

<table>
<thead>
<tr>
<th>$C_o$ (mg/L)</th>
<th>Temp. (°C)</th>
<th>$q_e$ (exp) (mg/g)</th>
<th>Pseudo-first order</th>
<th>Pseudo-second order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$k_1$ (min$^{-1}$)</td>
<td>$q_e$ (cal) (mg/g)</td>
</tr>
<tr>
<td>25</td>
<td>30</td>
<td>11.38</td>
<td>0.023</td>
<td>0.95</td>
</tr>
<tr>
<td>30</td>
<td>30</td>
<td>13.75</td>
<td>0.035</td>
<td>2.31</td>
</tr>
<tr>
<td>35</td>
<td>30</td>
<td>15.85</td>
<td>0.017</td>
<td>2.57</td>
</tr>
<tr>
<td>30</td>
<td>30</td>
<td>13.75</td>
<td>0.035</td>
<td>2.31</td>
</tr>
<tr>
<td>30</td>
<td>35</td>
<td>13.50</td>
<td>0.030</td>
<td>2.85</td>
</tr>
<tr>
<td>30</td>
<td>40</td>
<td>12.92</td>
<td>0.068</td>
<td>2.27</td>
</tr>
<tr>
<td>30</td>
<td>45</td>
<td>12.85</td>
<td>0.046</td>
<td>1.77</td>
</tr>
</tbody>
</table>

An analysis of data in Table 5.3, particularly the examination of agreement between $q_e$ (exp) and $q_e$ (cal) and the closeness of $R^2$ values towards unity at different initial concentrations and temperatures for both pseudo-first order and pseudo-second order models clearly reveal that pseudo-second order model fits better to the data. Therefore it is inferable that the adsorption of ErB dye on PSLW carbon can be well described by Lagergren pseudo-second order kinetics. Intuitively it implies that both the dye molecules and the functional groups on PSLW carbon are crucial in accomplishing the adsorption process. This observation is in agreement with the kinetics of adsorption of Direct Red 75 and Direct Red 80 dyes onto calcined bone reported by El Haddad et al. [34].
5.6 Intraparticle diffusion

To determine whether the intraparticle diffusion is the rate determining step or not the data are analyzed using Finkiam diffusion law. The intraparticle diffusion model is expressed as follows:

\[ q = k_i t^{1/2} + c \]  

(5.8)

where \( k_i \) is the intraparticle diffusion constant. In many adsorption processes adsorbate species transported from the bulk of the solution into solid phase through an intraparticle diffusion process and it can be the rate-limiting step [35].

Figure 5.14-Plots of intraparticle diffusion at different temperatures

Figure 5.14 depicts the plot of amount adsorbed (mg/g) versus \( t^{1/2} \), which are parabolic yet linear for some contact times at the initial stage and moreover they do not pass through origin. The intraparticle diffusion constant, \( k_i \), is the slope of the linear portion of the plot and the values obtained are 0.1744, 0.2712, 0.1594 and 0.2076 mg/g/min\(^{1/2}\) respectively at 30, 35, 40 and 45 °C. This pattern obviously indicates that the dye molecules in the first step get adsorbed onto the surface and slowly entered into the interior of the PSLW carbon particles through the pores [36] in the second step.
5.7 Mass transfer study

For any adsorption process, it is necessary to know the extent of transfer of adsorbate from the bulk to the surface of the solid adsorbent and at the interface of liquid and adsorbent particles. The findings in intraparticle diffusion are further substantiated by mass transfer equation. The external mass transfer was studied using the mathematical mass transfer model proposed by McKay et al. [37]. The McKay equation is,

\[
\ln \left[ \frac{C_L}{C_o} - \frac{1}{1+mk} \right] = \ln \left[ \frac{mk}{(1+mk) \cdot \frac{(1+mk)}{mk}} \right] \beta_L S_s t \quad (5.9)
\]

where \( m \) is the mass of adsorbent per unit volume of particle free solution (g/L), \( k \) (L/g) is the product of Langmiur constants \( Q_o \) and \( b \) while \( S_s \) is the outer surface area of adsorbent per unit volume of particle free slurry (cm\(^{-1}\)). The values of ‘\( m \)’ and \( S_s \) are calculated using the relations (5.10) and (5.11):

\[
m = \frac{W}{v} \quad (5.10)
\]

\[
S_s = \frac{6m}{(1-\varepsilon_p)d_p \rho_p} \quad (5.11)
\]

Figure 5.15-Plots of mass transfer at different temperatures
where \( W \) is the weight of adsorbent (g), ‘\( v \)’ is the volume of particle free adsorbate solution (L), \( d_p \) is the particle diameter (cm), \( \rho_p \) is the density of adsorbent (g/cm\(^3\)) and \( \varepsilon_p \) is the porosity of adsorbent particle. \( \beta_L \) is the mass transfer coefficient (cm/s).

The \( \ln [(C_t/C_o) – (1/1 + mk)] \) versus time plots are made (Figure 5.15).

**Table 5.4**-Mass transfer coefficients at different temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Mass transfer coefficient (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.0083</td>
</tr>
<tr>
<td>35</td>
<td>0.0065</td>
</tr>
<tr>
<td>40</td>
<td>0.0059</td>
</tr>
<tr>
<td>45</td>
<td>0.0054</td>
</tr>
</tbody>
</table>

It exhibits a linear behaviour indicating the rapid transport of dyes from bulk to solid phase. The mass transfer coefficient, \( \beta_L \) at different temperatures are calculated from the slope and intercept of the plots and are displayed in Table 5.4.

The mass transfer coefficients decrease with increase in temperature.

### 5.8 Column study

Column study was performed in order to make use of PSLW carbon for large scale treatment. Successful design of a column adsorption process requires a description of the dynamic behaviour of ErB dye in a fixed bed. Various mathematical models have been developed to describe and possibly predict the dynamic behaviour of the bed in column performance [38]. One such model used for continuous flow conditions is the Thomas model [39,40] which can be expressed in linear form as

\[
\log\left(\frac{C_o}{C_e} - 1\right) = \frac{k_d q M}{Q} - \frac{k C_o V}{Q} 
\]  

(5.12)
where $C_o$ and $C_e$ are the influent and effluent adsorbate concentrations respectively, $k$ is the Thomas rate constant (mL/min/mg), $q_o$ is the amount of solid phase solute (mg/g), $M$ is the mass of adsorbent (g), $Q$ is the influent flow rate (mL/min) and $V$ is the throughput volume (mL/min). The observed column data fit to the linearized form of the Thomas model. Figure 5.16 clearly displays the breakthrough curve for the adsorption of ErB dye on PSLW carbon (particle size 75 micron). Concentrations of effluent ErB dye is found to be zero for first 90 bed volumes, 90% of dyes is retained for next 20 bed volumes and 80% for another 10 bed volumes.

![Figure 5.16-Breakthrough curves for the adsorption of ErB dye on PSLW carbon](image)

After 120 bed volumes, the retention of ErB dye by the column gradually declines as the bed volume increases. The values of Thomas rate constant, $k$ and $q_o$ computed from the slope and intercept of the linear plot of $\log \left( \frac{C_o}{C_e} - 1 \right)$ versus $V$ at a given rate are found as $6.47 \times 10^{-2}$ (mL/min/mg) and 10.0 (mg/g) for ErB dye respectively. When the PSLW carbon was saturated with ErB dye, the latter was eluted with 500 mL of ethanol. Desorption study shows that the adsorbent can be reused and hence it is highly
economical. Thus, column analysis shows that PSLW carbon can be applied to the industrial process for the removal of dyes from aqueous solution.

5.9 Desorption study

Desorption studies were carried out to analyze the mechanism of adsorption and recovery of the adsorbent and adsorbate. The regeneration of the adsorbent may make the treatment process economical. Desorption of the adsorbed ErB dye was carried out using 0.1 N HCl, 0.1 N NaOH, CHCl$_3$ and ethanol. The percent desorption for ErB are found to be 22.1, 38.56, 7.28 and 26.8 respectively with 0.1 N HCl, 0.1 N NaOH, CHCl$_3$ and ethanol.

5.10 Conclusion

The present study shows that PSLW carbon is a very promising low cost adsorbent for the effective removal of ErB dye from aqueous solution. Adsorption data fitted well with the Langmuir isotherm shows the monolayer coverage of the adsorbate on the surface of the adsorbent. From the thermodynamic studies, the adsorption of ErB dye on PSLW carbon is found to be spontaneous, exothermic and thermodynamically favorable at low temperature. The kinetic data agree well with the pseudo-second order rate equations with multi-step intraparticle diffusion method. Thomas model is effectively used to predict the removal of ErB dye. From the results it is concluded that the adsorption of ErB dye onto the surface involves a faster adsorption followed by slow diffusion into internal sites through pores. Thus, application of this PSLW carbon may be highly useful in designing the cost effective and highly efficient technique for textile industrial effluent treatments.
References


40. T.D. Reynolds and P.A. Richards, Unit operations and processes in Environmental Engineering, PWS, Boston, USA, 142 (1996).