Comparative Study between Experimental and Simulated Breakthrough Curve for the Removal of Methylene Blue from Wastewater

Ahmad Hasan Nury*,1, Md.Jahir Bin Alam2, Md. Imran Kabir*1
1 Department of Civil Engineering, Leading University, Sylhet, Bangladesh
2 Department of Civil and Environmental Engineering, Shahjalal University of Science and Technology, Sylhet, Bangladesh

Corresponding Author: hasancee@yahoo.com

ABSTRACT

Computer simulation is necessary while the performance of dynamic experiments is not feasible. In this study, a breakthrough curve was formulated for the removal criteria of Bombax Ceiba over Methylene Blue. The performance of packed bed adsorbent (activated carbon of Bombax Ceiba) was discussed by the breakthrough curve. Concentration, time interval, volumetric water content, dispersivity, distribution coefficient, retardation factor, flux density, bulk density and depth increment were chosen in account as the simulation parameters. Both batch and column studies were done. In column, after comparing the simulated breakthrough curve with experimented one, the effluent concentration was found zero after 120min, 180min and 270min for the adsorbent bed 15cm, 20cm and 25cm respectively. Admittedly, the breakpoint time for 15, 20 and 25cm were nearly at 158, 169 and 198min accordingly whereas the respective bed exhaustion time were 270min, 360min and 420min. Finally, satisfactory fitness of the simulated breakthrough curve with the experimented one was established.

Keywords: Simulation, Adsorption, breakthrough curve, Methylene Blue, Wood charcoal of Bombax ceiba

1. INTRODUCTION

Water pollution due to colour from dye-stuff industries is a topic of major concern of scientists today. Many industries use dyes extensively in different operations such as textile, paper, plastic, leather tanning etc. Dyes exhibit considerable structural diversity [1]. Dyes are commonly found in trace quantities at industrial scale and in industrial effluents. It is a fact that due to their visibility, dyes are recognized easily even at the levels as less as 1ppm [2]. The discharge of color waste is not only damaging the aesthetic nature of receiving streams but also wide-spreading toxicity to aquatic life [3]. In addition, color interferes with the transmission of sunlight into the stream and therefore reduces photosynthetic action. Toxicity of dyes to fauna and flora is well documented [4].

Dyes also inhibit several biological processes. Colour of textile effluents escalates environmental problem mainly because of its non-biodegradable characteristics [5]. The removal of dye in an economic fashion remains an important problem. Considerable work has been carried out on the removal of dye from wastewater by adsorption, coagulation, flocculation, oxidation, precipitation filtration, electrochemical processes, etc are the common techniques reported for the removal of dyes from effluents [6]. Chemical methods of dye removal accumulate sludge that can create disposal problems. These methods require chemicals and require large amount of electrical energy which further poses problems for environment. Processes such as membrane separation, coagulation and ion exchange are also used for the removal of color from dye wastewater, but the cost of the process is the main drawback of these techniques. Amongst the techniques, adsorption seems to be one of the most effective methods because of simple operation and easy handling [7]. Different adsorbents such as zeolite, perlite, benotite, kaolite, rice husk, maize cob, coconut coir, bagasse pith, etc. have been employed for removal of dyes from effluents.

The purpose of the study was to remove Methylene Blue from aqueous solution using wood charcoal of Bombax Ceiba. Wood charcoal adsorption treatment process has been proven to be an effective replacement for the combined biological and chemical treatment [8]. The performance of wood charcoal treatment process depends on the type of charcoal and the characteristic of the wastewater in addition to the operating conditions. By interfacing a process simulation, a realistic environment can be created without the cost. It can be used to predict the behavior of the process under different conditions.

2. METHODOLOGY

To disaggregate the wood material, the collected Bombax Ceiba was boiled at 100°C in a 10% Phosphoric acid (H₃PO₄) for 1h. After the pre-treatment, the solution was kept at room temperature for 24h and also burned afterward at 400°C as well as crushed and passed through 0.6μm sieve to get the activated carbon from the wood charcoal.

Batch study was performed in five 250ml stopper bottles to determine the equilibrium adsorption parameters. In each bottle 200ml of dye sample of five different concentrations, 1 to 5mg/l was poured. A fixed amount of adsorbent is added to each solution. The samples are then shaken with a flask shaker at 450 osc for 8-10 hrs. Within this time the system reaches equilibrium. The solutions are then centrifuged for 10-15min to settle down the adsorbent. The dye solution is then separated and the concentration of the solution is determined with UV-vis spectrophotometer at 455nm wavelength [9].
The Langmuir adsorption isotherm [10] for solid-liquid adsorption system is represented by the following equation:

\[
\frac{1}{q_e} = \frac{1}{q_\infty K} \cdot \frac{1}{C_e} + \frac{1}{q_\infty}
\]

where, \(q_e\) is the adsorption density at equilibrium (Kg adsorbate/Kg adsorbent), \(C_e\) is the equilibrium concentration of the adsorbate in the solution (Kg/m^3), \(q_\infty\) is the adsorption capacity (Kg adsorbate/Kg adsorbent) and \(K\) is an empirical constant (m^3/Kg).

Fixed bed column studies were conducted in a glass cylindrical column. The column was designed with an internal diameter of 6.5 cm and 45 cm in length. The column was packed with adsorbent between two supporting layers of glass wool. The dye (methylene blue) containing wastewater was passed through column in regulated flow by rotameter. The samples were collected at certain time intervals and the concentration of dye was determined spectrophotometrically by monitoring of the absorbance at 455 nm. Schematic diagram for the experimental procedure are shown in Fig. 1.

![Fig. 1: Schematic diagram for experimental method to treat colored water](image)

Table 1: Experimental variable for 15 cm bed height

<table>
<thead>
<tr>
<th>Initial dye concentration</th>
<th>15ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount of absorbent</td>
<td>80gm</td>
</tr>
<tr>
<td>Flow rate</td>
<td>20 ml/min</td>
</tr>
</tbody>
</table>

Table 2: Experimental variable for 20 cm bed height

<table>
<thead>
<tr>
<th>Initial dye concentration</th>
<th>10ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount of absorbent</td>
<td>120gm</td>
</tr>
<tr>
<td>Flow rate</td>
<td>25 ml/min</td>
</tr>
</tbody>
</table>

Table 3: Experimental variable for 25 cm bed height

<table>
<thead>
<tr>
<th>Initial dye concentration</th>
<th>10ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount of absorbent</td>
<td>160gm</td>
</tr>
<tr>
<td>Flow rate</td>
<td>30 ml/min</td>
</tr>
</tbody>
</table>

Temperature of 26±2°C and pH of 6.8 as were used for this study. The experimental breakthrough curve are presented in fig:2 with simulated one.

**MATHEMATICAL FORMULATION FOR THE SIMULATION**

A sorbing chemical is being moved through a homogeneous medium at a study, uniform flow rate, the transport equation [11] and [12] can be written as

\[
\frac{c - \rho \frac{\partial s}{\partial t}}{\theta \rho} + D \frac{\partial^2 s}{\partial x^2} = \frac{\partial}{\partial x} \left( \frac{-v s}{\rho} \right)
\]

where, \(c\) = volume averaged concentration, \(s\) = amount of solute adsorbed, \(D\) = dispersion coefficient, \(v\) = pore water velocity, \(\theta\) = volumetric water content, \(\rho\) = bulk density, \(x\) = distance and \(t\) = time. The first term represents accumulation of solute in the liquid. The second term in the left hand side of the equation describes the chemical interaction. The third term represents axial dispersion of solute in the bed, which leads to mixing of the solute and solvent. Last term of the equation is the amount of solute flowing in by convection to the section \(dx\) of the bed minus that flowing out. The equation can be rearranged to yield as

\[
\frac{c - \rho \frac{\partial s}{\partial t}}{\theta \rho} = R(c) \frac{\partial s}{\partial t}
\]

where, \(R\) is the retardation factor, \(R(c) = 1 + \frac{\theta D}{\rho L}\).

As seen, \(R(c)\) can be explicitly written if a relationship between \(s\) and \(c\), called the sorption isotherm is available. For brevity, a detailed description of the sorption isotherm will be presented in the following section.

A general relationship that combines an isotherm function \(\Gamma\), describing sorption to a homogeneous surface at the stoichiometric level and a weighing function \(\omega\), describing the effects of site specific binding is written as

\[
\frac{S_T}{S_T} = \int_0^{\xi} \omega(\xi) \Gamma(c, \xi) d\xi = f(c)
\]

where, \(S_T\) is the total amount of sorption sites and \(\xi\) is an affinity coefficient. Various isotherms for sorption are then derived by choosing appropriate functional forms for \(\Gamma\) and \(\omega\). For example a generalized Langmuir-Freundlich isotherm,

\[
S = \frac{S_T}{1 + \frac{c}{K}}
\]

is derived by choosing

\[
\Gamma(c, \xi)\frac{c}{1 + \xi c}
\]

and

\[
\omega(\xi) = \frac{\sin(n\xi)}{n(k^2 \xi^2 - 2 \cos(n\xi) - K^2 \xi^2)}
\]

where \(k\) and \(\alpha\) are constants. The retardation factor thus can be written as
Thus the governing equation in the tri-diagonal form can be written as

\[ R(C) = 1 - \frac{\rho K_F}{\theta} \left[ \frac{\theta}{1-(\theta C)^n} \right]^2 \]

For \( i = 1 \) and \( i = m \), the above equation can be written as follows

\[ \left( \frac{D}{\theta} \right) \frac{V}{2} C_i - \left( \frac{2D}{\theta} \right) C_{i+1} \left( \frac{V}{2} \right) C_i = -\frac{K_F C_i}{\theta} \]

where, \( \rho \) is bulk density, \( K_F \) is distribution coefficient, \( \theta \) is volumetric water content, \( D \) is dispersivity, \( v \) is the flux density and \( R \) is retardation factor.

For simulation, Pascal Programming software was used. The variables are bed height (15cm, 20cm and 25cm), initial concentration of the dye solution (10mg/l, and 15mg/l) and flow rate (20 ml/min, 25ml/min and 30ml/min). The system considered was an isothermal adsorption column packed with porous adsorbent (wood charcoal of \textit{Bombax ceiba}). The simulated breakthrough curve was drawn from the output of the simulation and compared with the experimental breakthrough curve. The used parameters are given in Table 1.

Table 4: Parameters used in the simulation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volumetric water content, ( \theta )</td>
<td>0.5</td>
</tr>
<tr>
<td>Dispersivity, ( \lambda ), cm</td>
<td>0.5</td>
</tr>
<tr>
<td>Distribution coefficient</td>
<td>2.0</td>
</tr>
<tr>
<td>Time interval, min</td>
<td>30</td>
</tr>
<tr>
<td>Flux density, cm/h</td>
<td>5.0/24.0</td>
</tr>
<tr>
<td>Bulk density, ( \rho ), g/cm³</td>
<td>1.2</td>
</tr>
<tr>
<td>Alpha, ( \alpha )</td>
<td>0.8</td>
</tr>
<tr>
<td>Omega, ( \omega )</td>
<td>20</td>
</tr>
</tbody>
</table>

3. RESULTS AND DISCUSSION

The comparison between the simulated and experimental breakthrough curve are given in Fig. 2.

From the above figures, it is clearly seen that relative concentrations are zero around 120min, 180min and 270min respectively. This is because initially the solutes are adsorbed by pore space of adsorbent. After this time the concentration rise slowly up to 157.5min, 168.9min and 198.3min for 15cm, 20cm and 25cm bed height respectively which is called the break point. Most of the bed capacity is used at the break point. This point is the level of permissible limit of water parameter. It increases at higher bed height. Because pores take more time to adjust for higher bed depth. After the break point time is reached, the outlet concentration rises very rapidly up to point of bed exhaustion. This is because particles were adjusted and the pores between the particles reduced to adsorb. The bed exhaustion time for 15cm, 20cm and 25cm bed are 270min, 360min and 420min respectively. At bed exhaustion time the bed is considered as ineffective.

4. CONCLUSION

For simulated & experimental breakthrough curve of bed height 20 cm (initial concentration 10mg/l and flow rate 25 ml/min), relative concentrations are zero up to 180min, breakpoint time is 168.9min and bed
exhaustion time is 360min. For simulated & experimental breakthrough curve of bed height 25 cm (initial concentration 10mg/l and flow rate 30 ml/min) relative concentrations are zero up to 270min, breakpoint time is 198.3min and bed exhaustion time is 420min. So the agreement between the experimental and the simulated breakthrough curves appear to be satisfactory since the simulated results obtained agreed with the experimental results. Comparing simulated breakthrough curve with experimental breakthrough curve of bed height 15 cm (initial concentration 15mg/l and flow rate 20 ml/min), it is seen that for both curve relative concentrations are zero up to 120min, breakpoint time is 157.5min and the bed exhaustion time for simulated & experimental breakthrough curve are 270min & 300min respectively. The simulated breakthrough curve will be helpful to design the adsorption column for dye removal operation.

ACKNOWLEDGEMENT

The authors would like to record gratitude to Shahjalal University of Science and Technology, Sylhet, Bangladesh for providing the Laboratory facilities for this research.

REFERENCES


APPENDIX-I

Computer programme to simulate breakthrough curve

Program solute_nonlinear;
{$N+}
{$D+, L+}
uses crt;

| Nodal scheme ----------------------------- i = 0 surface
|------------------------------- i=1
|------------------------------- i=2
|       
|------------------------------- i = m Lower
boundery }
const
eqn       = 500;
Ci          = 0.0;
Tzero     = 5.0 * 24.0;
theta       = 0.5
Lambda  = 0.5
K_F        = 2.0;
flux         = 5.0 / 24.0;
rho         = 1.2;
ddepth    = 0.2499975;
stime      = 30.0 * 24.0;
ptime      = 24.0;
dtime      = 0.05 x 24.0;
type
 precision       = Real;
arraytypeone  = ARRAY [1…eqn, 1…3] OF Precision;
arraytypetwo  = ARRAY [1…eqn] OF Precision;
var
D                     : Precision;
V                      : Precision;
Czero               : Precision;
ConcNew         : arraytypetwo;
ConcOld          : arraytypetwo;
time                 : Precision;
matrix              : arraytypeone;
size                 : integer;
k, iter               : integer;
Q,U,T              : Precision; {Dummy variables}
R                     : Arraytypetwo;
Outfile              : string;
OutData            : text;
Procedure Diagonal (var m : ArrayTypeOne; var s : ArrayTypeTwo; var n : integer);
var
  multiplier : Precision;
  i,j          : integer;
being
  { forward pass }
  for i := 2 to n do
begin
  multiplier := m[i,1] / m[i-1, 2];
  m[i, 2] := m[i,2] - multiplier * m[i-1, 3];
  s[i] := s[i] - multiplier * s[i-1];
end;
{backward pass}
S[n] := s[n] / m[n,2];
for i := (n-1) downto 1 do
  s[i] := (s[i] – m[i,3] * s[i+1] ) / m[i,2];
end;
FUNCTION Retardation ( Concentration : Extended ) : Extended;
{********** Retardation **********}
Const
  alpha = 0.8;
  omega = 20.0;
begin
  if Concentration = 0.0 then
    Retardation := 1.0
  else
    Retardation := 1.0 + rho * K_F * alpha / theta * exp ((alpha – 1.0) * ln (Concentration));
end;
{********** ALTERNATIVE **********}
{ begin
  If concentration = 0.0 then
    Retardation := 1.0
  else
    Retardation := 1.0 + ( rho * K_F * alpha / theta) * exp ((alpha – 1.0) * ln (Concentration)) / sqr (1.0 + exp ( alpha * ln (omega * concentration) ) );
end; }
{ Function Retardation ends}
{BEGIN MAIN ALGORITHM}
begin
  clrscr;
  { open an ASCII file for output}
  Writeln (' Enter a name and path to create an ASCII output file');
  Readln (Outfile);
  Assign (OutData, OutFile); Rewrite (OutData);
  writeln ( Retardation (0.0000) : 5 : 2);
  readln;
  v := flux / theta;
  D := Lambda * v;
  for k := 1 to eqn do
    ConcOld[k] := Ci;
  {Time stepping stars}
  time := dt ime
  while time < stime do
  begin
    if time < Tzero then
      Czero := 0.0;
    else
    begin
      for iter := 1 to 2 do
      begin
        if iter = 1 then
          for k := 1 to eqn do
            R[k] := Retardation (ConcOld[k]);
      {********** second iteration **********}
      else
        for k := 1 to eqn do
          R[k] := Retardation (ConcNew[k]);
      end;
      P := (D / ddepth – 0.5 *v ) / ddepth;
      U := (D / ddepth + 0.5 * v) / ddepth;
      {Setup coefficient matrix}
      for k := 1 to eqn do
        begin
          matrix[k,1] := U;
          matrix[k,2] := - (2.0 * D / (ddepth * ddepth) + R[k] / dtime);
          matrix[k,3] := p;
        ConcNew[k] := Retardation (ConcOld[k]) / dtime * ConcOld[k];
      end;
      Matrix[eqn,2] := p – (2.0 * D / (ddepth * ddepth ) + R[eqn] / dt ime);
      size := eqn; {pass the constant eqn to an integer type variable for passing to the procedure diagonal}
      diagonal (matrix , ConcNew , size);
    end;
    if round (time) mod round (ptime)  = 0 then
      Writeln (Outdata, 60 * ddepth : 12:3, Time / 24.0 : 12 :2,
      ConcNew[60] : 10 : 4 );
    for k := 1 to eqn do
      ConcOld[k] := ConcNew[k];
    time := time + dt ime;
    end;
    Close (OutData);
  end.