Utilization of *Euryale ferox* Salisbury seed shell for removal of basic fuchsin dye from water: Equilibrium and kinetics investigation

S. Kalita,* M. Pathak,* G. Devi,* H. P. Sarma,‡ K.G. Bhattacharyya,§ A. Sarma∥ and A. Devi,* *

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**APPENDIX**

**Adsorption isotherm and kinetic models studied for *E. ferox***

In the present study, the adsorption data were subjected to different isotherm and kinetic models for examining and understanding the mechanistic steps and surface chemistry involved in the adsorption process. The thermodynamic behavior was also extensively studied.

Equations (1)-(8) are used to verify the isotherm models for the adsorption study of basic fuchsin dye on *E. ferox*:

The Langmuir isotherm in the linear equation form is expressed as:

\[ \frac{C_e}{q_e} = \left( \frac{1}{b q_m} \right) + \left( \frac{C_e}{q_m} \right) \]

where \( C_e \) and \( q_e \) are the equilibrium liquid phase and solid phase concentrations of the dye respectively, \( b \) (L mg\(^{-1}\)) is the Langmuir constant and \( q_m \) (mg g\(^{-1}\)) is the amount of dye adsorbed per unit mass of the adsorbent in a single monolayer. \( q_m \) and \( b \) were calculated from the slope and intercept of the plot between \( C_e/q_e \) versus \( C_e \). The occurrence of a favourable or unfavourable adsorption can be determined using Hall separation factor \( R_L \) which is defined by the equation,

\[ R_L = \frac{1}{(b C_e)} \]

On the basis of four conditions of \( R_L \) values the adsorption process can be determined as: i) favourable, 0<\( R_L <1 \), ii) linear, \( R_L = 1 \), iii) unfavourable: \( R_L > 1 \), iv) irreversible, \( R_L = 0 \).

The Freundlich isotherm in its linear equation form is written as:

\[ \log q_e = \log K_f + n \log C_e \]

where \( C_e \) (mg L\(^{-1}\)) is the dye concentration at equilibrium, \( q_e \) (mg g\(^{-1}\)) is the adsorption capacity at equilibrium, \( K_f \) (mg g\(^{-1}\)) (L g\(^{-1}\))\(^n\) and \( n \) are Freundlich constants related to distribution coefficient and sorption intensity of adsorbents respectively. The plot
between log \(q_e\) against log \(C_e\) was used for calculating Freundlich constants. The adsorption process is implied as favourable when the value of \(n\) lies in the range of 1-10 (0<1/n<1).\(^5\)\(^6\)

The equation for Temkin isotherm is stated as\(^7\):

\[
q_e = B \ln KT + B \ln C_e
\]

\[
B = \frac{RT}{b}
\]

where \(q_e\) (mg g\(^{-1}\)) is the adsorption capacity at equilibrium, \(B\) (J mol\(^{-1}\)) is the Temkin constant related to the heat of sorption, \(A\) (L g\(^{-1}\)) is the equilibrium binding constant corresponding to the maximum binding energy, \(C_e\) (mg L\(^{-1}\)) is the dye concentration at equilibrium, \(R\) (8.314 J mol\(^{-1}\) K\(^{-1}\)) the gas constant, \(T\) (K) is the temperature and \(b\) (KJ mol\(^{-1}\)) is the Temkin isotherm constant. A plot of \(q_e\) versus log \(C_e\) enabled the determination of the isotherm constants \(B\) and \(A\) from the slope and the intercept respectively.

The linear form of Dubinin and Radushkevich\(^8\) isotherm is expressed as:

\[
ln (q_e) = ln (q_s) - K_{ad} \varepsilon^2
\]

\[
\varepsilon = RT ln (1 + 1 / C_e)
\]

where \(q_s\) (mg g\(^{-1}\)) is the D-R monolayer adsorption capacity, \(K_{ad}\) (mol\(^2\) KJ\(^{-2}\)) is the D-R isotherm constant, \(\varepsilon\) is the Polanyi potential (J mol\(^{-1}\)), \(R\) is the gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)), \(T\) is the absolute temperature (K), and \(C_e\) (mg L\(^{-1}\)) is the dye equilibrium concentration. The mean free energy of biosorption, \(E\), is the energy per molecule of solute when transferred from the infinite solution concentration to the surface of the adsorbent. It is calculated from \(K_{ad}\) using the equation:

\[
E = \frac{1}{\sqrt{2}K_{ad}}
\]

The linear equation of the first order model\(^9\) and second-order kinetic equation\(^10\) is represented respectively as:

\[
\log (q_e - q_t) = \log q_e - (k_1 / 2.303) t
\]

\[
t / q_t = 1 / k_2 q_22 + t / q^2
\]

where \(q_e\) (mg g\(^{-1}\)) and \(q_t\) (mg g\(^{-1}\)) are the amounts of the adsorbate adsorbed on adsorbent at equilibrium and time \(t\) (min), \(k_1\) (min\(^{-1}\)) is the equilibrium rate constant of first order adsorption, \(q_2\) (mg g\(^{-1}\)) is the maximum adsorption capacity, \(k_2\) (g mg\(^{-1}\) min\(^{-1}\)) is the rate constant of second order adsorption.

The Elovich equation is expressed as\(^11\):

\[
q_t = \beta \ln (\alpha \beta) + \beta \ln (t)
\]

where the constants initial adsorption rate, \(\alpha\) (mg g\(^{-1}\) min\(^{-1}\)) and desorption constant, \(\beta\) (g mg\(^{-1}\)) are calculated from the slopes and intercepts of plots \(q_t\) against \(\ln t\).

The equation which defines the intraparticle diffusion model variables is as follows\(^12\):
\[ qt = k_p t^{0.5} + C \]  

where \( k_p \) is the intraparticle diffusion rate constant (mg \( \cdot \) g\(^{-1} \) \( \cdot \) min\(^{-1/2} \)), and \( C \) is the intercept.

The liquid film diffusion model is represented as follows\(^{13}\):

\[ \ln (1 - F) = -k_{fd} t \]  

where \( F \) is the fractional attainment of equilibrium (\( F = \frac{q_t}{q_e} \)), \( k_{fd} \) (min\(^{-1}\)) is the liquid film diffusion constant.

**Thermodynamic parameters**

The thermodynamic parameters such as a change in Gibbs free energy (\( \Delta G \)), change in enthalpy (\( \Delta H \)) and change in entropy (\( \Delta S \)) were calculated by using following equations\(^{14}\):

\[ \Delta G = -RT \ln K_L \]  

\[ \ln K_L = -\Delta G/RT = \Delta S/R - \Delta H/RT \]  

where \( R \) represents the gas constant (8.314 J \( \cdot \) mol\(^{-1} \) \( \cdot \) K\(^{-1} \)), \( T \) is the absolute temperature (K) and \( K_L \) is the Langmuir equilibrium constant. The plot of \( \ln K_L \) versus \( 1/T \) was used to calculate \( \Delta H \) and \( \Delta S \) values from the slope and intercept of this plot respectively.

**PHASE CONTRAST AND SEM MICROGRAPHS**
**Fig. 15.** (a) Phase contrast microscopic images of *E. ferox* negative control (b) Phase contrast microscopic images of *E. ferox* test after dye adsorption (c) SEM micrograph of *E. ferox* negative control (d) EDX image of *E. ferox* negative control (e) SEM micrograph of *E. ferox* test after dye adsorption (f) EDX image of *E. ferox* test.

**REFERENCES**


