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

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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[1] in the linear equation form is expressed as:

$$Ce/qe = (1/bqm) + (Ce/qm) \quad (1)$$

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,

$$RL = 1/(bCe) \quad (2)$$

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, $R_L= 0$. [2,3]

The Freundlich isotherm[4] in its linear equation form is written as:

$$log\ qe = log\ Kf + n\ log\ Ce \quad (3)$$

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]:

$$qe = B \ln KT + B \ln Ce \quad (4)$$

$$B = RT/b \quad (5)$$

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:

$$\ln (qe) = \ln (qs) - Kad.\varepsilon 2 \quad (6)$$

$$\varepsilon = RT \ln (1 + 1/Ce) \quad (7)$$

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, ε 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:

$$E = 1/\sqrt{2Kad} \quad (8)$$

The linear equation of the first order model[9] and second-order kinetic equation[10] is represented respectively as:

$$\log (qe - qt) = \log qe - (k1/2.303)\, t \quad (9)$$

$$t/qt = 1/k2q22 + t/q2 \quad (10)$$

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]:

$$q_t = \beta \ln (\alpha\beta) + \beta \ln (t) \quad (11)$$

where the constants initial adsorption rate, α, (mg $g^{-1}min^{-1}$) and desorption constant, β, (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]:

$$qt = kpt^{0.5} + C \quad (12)$$

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

The liquid film diffusion model is represented as follows[13]:

$$ln\,(1 - F) = -\,kfd.t \quad (13)$$

where F is the fractional attainment of equilibrium (F = qt/qe), k_{fd} (min^{-1})is the liquid film diffusion constant.

Thermodynamic parameters

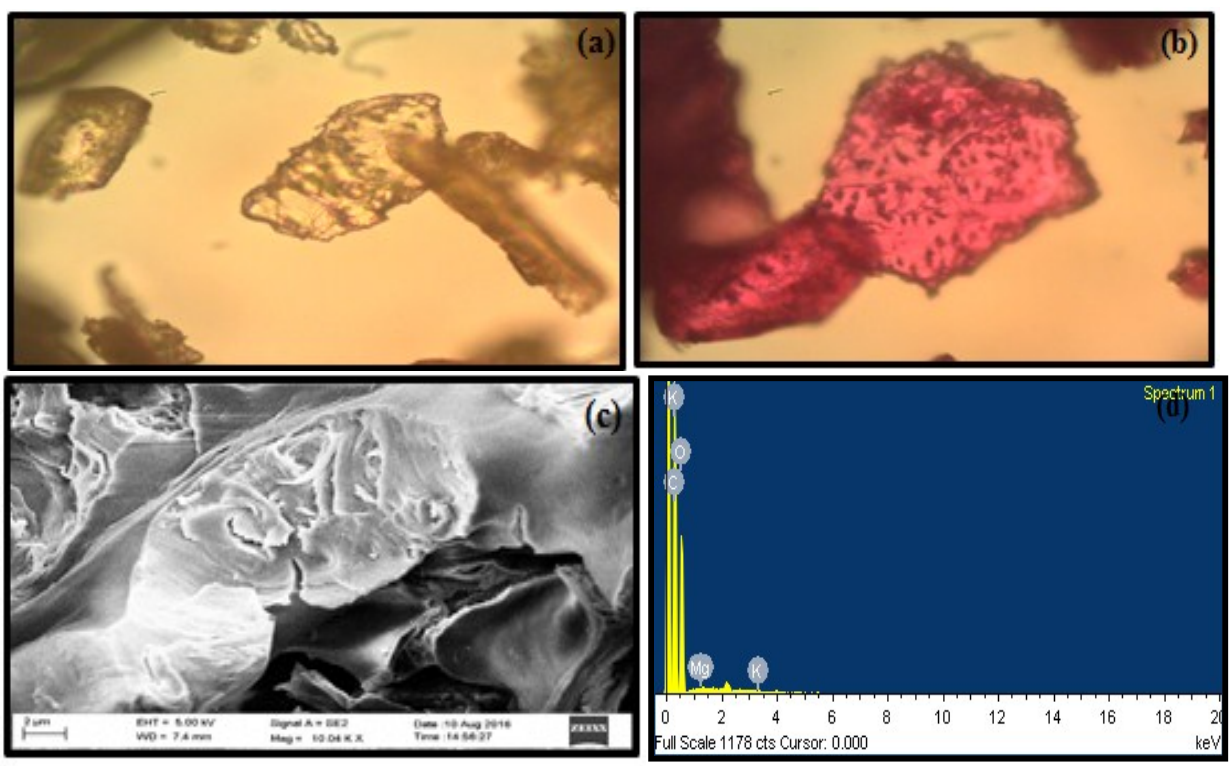
The thermodynamic parameters such as a change in Gibbs free energy (ΔG), change in enthalpy (ΔH) and change in entropy (ΔS) were calculated by using following equations[14]:

$$\Delta G = -\,RT\,ln\,KL \quad (14)$$

$$ln\,KL = -\Delta G/RT = \Delta S/R - \Delta H/RT \quad (15)$$

where R represents the gas constant (8.314 J mol^{-1}. 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 ΔH and ΔS values from the slope and intercept of this plot respectively.

PHASE CONTRAST AND SEM MICROGRAPHS



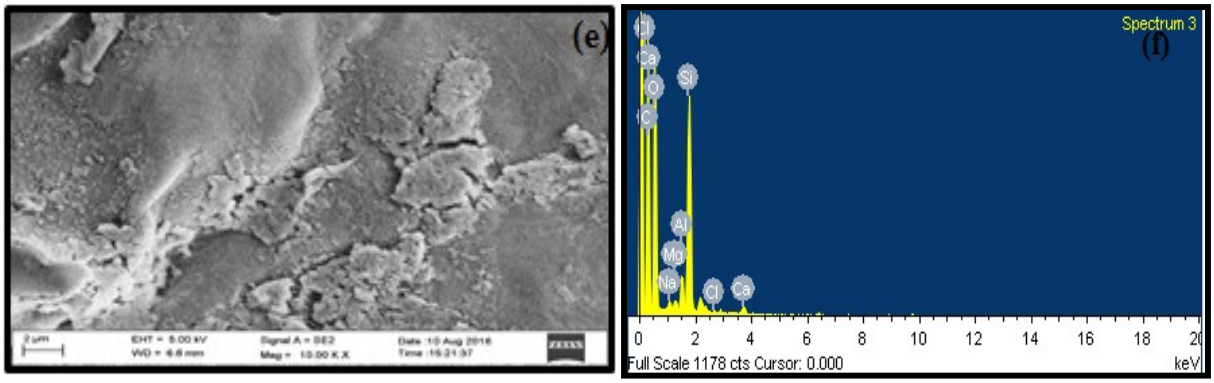


Fig.1S. (a) Phase contrast microscopic images of *E. ferox* negative control (b) Phase contrast microscopic images of *E. ferox* test after dye adsorption (c) SEM micrograph of *E. ferox* negative control (d) EDX image of *E. ferox* negative control (e) SEM micrograph of *E. ferox* test after dye adsorption (f) EDX image of *E. ferox* test.

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