SUPPLEMENTARY MATERIAL

Review

Valorization of Eggshell as Renewable Materials for Sustainable Biocomposite Adsorbents – An Overview

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Section S1: Equilibrium Isotherm Models

Langmuir: The Langmuir model is the simplest model to explain adsorption process on monolayer adsorption surface where adsorption energy is constant over the whole surface area and all sites on the adsorbent surface have equal adsorption energy that are considered as independent adsorption sites [85,86]. The Langmuir model is described by the relationships in Equations S1 (nonlinear) and S2 (linear) in Table S1.

Freundlich: The Freundlich model is semi-empirical in nature and provides an account of multilayer adsorption onto a heterogeneous surface, the enthalpy of adsorption is a variable value that also depends on the degree of surface coverage, with various interactions among adsorbed species [63]. The linear and non-linear forms of the Freundlich model are expressed by Equations S3 and S4 respectively in Table S1.

Temkin: The Temkin isotherm model described respectively by Equations S5 and S6 in Table S1 describes the adsorption isotherm for an adsorbent/adsorbate system by its nonlinear and linear forms. It assumed there is linear decrease in heat of adsorption of all adsorbates in the layer with increasing surface coverage because of lateral interactions between adsorbates and that adsorption is characterized by a uniform distribution of binding energies, up to some maximum value [87]

Dubinin-Radushkevich (D-R): The D-R model can be used to for adsorption processes onto homogenous and heterogenous surfaces. It is used to estimate characteristic porosity and the apparent free energy of adsorption [88,89], according to the non-linear and linear forms of the isotherm respectively shown by Equations S7 and S8 in Table S1.

Redlich-Peterson (R-P): The R-P isotherm model is an empirical hybrid expression based on the Langmuir and Freundlich models. it could be applied to both homogenous and heterogeneous adsorption [90]. The nonlinear isotherm model is described by Equation S9 in Table S1.

Sips: This is another hybrid form of the Langmuir-Freundlich models that is often considered as a popular isotherm model that contains 3-parameters, which accounts for monolayer adsorption profiles. The Sips model [91] can describe a range of processes for adsorbents with homogenous and heterogeneous adsorption sites, according to the exponential term described in Equation S10 in Table S1.

Harkins-Jura (H-J): The H-J model also is used to describe multilayer adsorption processes that accounts for the presence of a heterogeneous pore distribution [63]. The non-linear form of the isotherm is shown by Equation S11 in Table S1.

Section S2: Kinetic models

Pseudo first order (PFO): The Lagergren kinetic equation also known as, pseudo first-order (PFO) model, is more suitable with low solute concentrations, and it is represented by the Equations S12 and S13 in Table S2.

Pseudo second order (PSO): In 1999, Ho and McKay, [96] adopted the pseudo-second order (PSO) model to explain sorption kinetics and this model is assumed to be applicable for chemisorption processes. The non-linear and linearized forms are shown in Equations S14 and S15 in Table S2.

Intra-particle diffusion (IPD): This model proposed by Weber-Morris, represented in Equation S16 in Table ES2, assumes that for many adsorption processes, solute uptake varies almost proportionally with $t^{1/2}$ rather than with the actual contact time t. If ID occurred, the plot will be linear and if IPD is the only rate limiting step, the plot will pass through the origin [92].

Elovich: This model has found application in a range of slow rate adsorption processes, and it is generally applicable in chemisorption kinetics, [97] as described by Equation S17 in Table S2.

For the case of industrial or other large-scale operations, adsorption processes are carried out in continuous fixed bed columns where dynamic adsorption process occur. The polluted-influent stream is purified as it passes through the column packed with the fixed bed of adsorbent particles and at the exit of the column, it is released as the effluent. The efficiency of such systems can be analyzed through a breakthrough curve, which is a plot of adsorbate concentration against time of exit at the column [94]. Various mathematical models such as the Thomas, Bed Depth Service Time (BDST), Yoon-Nelson, Adams and Bohart, Wolborska, Clark, Modified Dose Response were applied for the evaluation and applicability of column beds for adsorption of pollutants. Some of those discussed in this overview are highlighted below:

Thomas: The Thomas model was proposed on the assumption of Langmuir kinetics of adsorption-desorption that rate driven forces follow second-order reversible reaction kinetics [95,98]. This model is suitable for adsorption process where there are negligible interferences from external and internal diffusion resistances [99]. The Thomas model equation is as shown with its non-linear (Equation S18) and linear (Equation S19) forms in Table S2.

Adams-Bohart: This is perhaps the mostly applied model to fixed bed column, it is a simplified solution for the rigorous mass balance equation that assumes a negligible axial dispersion and that the form of the rate profile is equivalent to a rectangular isotherm ([94]. Adams-Bohart model proposed that adsorption rate is dependent upon the concentration of adsorbing species and residual capacity of adsorbent [95,100]. The non-linear (Equation S20) and linear (Equation S21) forms are represented as shown in Table S2.

Bed Depth Service Time (BDST): BDST model works on the assumption that adsorption rate is controlled by the surface reaction between adsorbate and the unused capacity of the adsorbent, ignoring resistances from external film and intraparticle diffusion mass transfer [95,101]. The BDST model is expressed by Equation S22 in Table S2.

Yoon-Nelson: Yoon-Nelson model is respectively shown by the non-linear and linear models in Equations S23 and S24 shown in Table S2, which is based on the assumption that decreasing rate of adsorption is directly related to adsorption of the adsorbate and breakthrough from the adsorbent [95].

Table S1: Adsorption Isotherm models and parameters

Models	Parameters
Langmuir Isotherm $q_e = \frac{k_L q_{max} C_e}{1+ k_L C_e}$ Equation S1 $\frac{C_e}{q_e} = \frac{1}{k_L q_m} + \frac{C_e}{q_m}$ Equation S2	equilibrium adsorption capacity (q_e; mg/g); concentration of adsorbate in solution at equilibrium (C_e; mg/L); Langmuir equilibrium constant (K_L; L mg^{-1}) that is characteristic of the affinity between the adsorbate and adsorbent; the maximum adsorption capacity (q_{max}; mg/g).
Freundlich Isotherm $q_e = k_F C_e^{1/n}$ Equation S3 $og\, q_e = log k_F + \frac{1}{n} log C_e$ Equation S4	q_e and C_e (mg/L) are similarly defined as in Equations (1-2) above; k_F and n are Freundlich Isotherm constants, k_F (mg$^{(1-1/n)}$ L$^{1/n}$/g) is the adsorption capacity while n, a dimensionless factor, is the intensity of the adsorption process, which provides an indication of the surface heterogeneity of the adsorbent
Temkin Isotherm $q_e = \frac{RT}{b\, ln\,(k_T C_e)}$ Equation S5 $q_e = B \ln (k_T) + B\, ln\, (C_e)$ Equation S6	q_e (mg/g) and C_e (mg/L) are similarly defined as in Equations (1-2); B = RT/b; b (J mol^{-1}). The Temkin constant; k_T (L/mg), an equilibrium binding constant relating to maximum binding energy; R (J/mol K) = the universal gas constant; T (K) = temperature, B = constant related to heat of the adsorption process.
Dubinin-Radushkevich (D-R) $q_e = q'_m \exp(-k_{DR} \varepsilon^2)$ Equation S7 $\ln(q_e) = \ln(q'_m) - k_{DR} \varepsilon^2$ Equation S8	q_e (mg/g) is defined as in Equations (1-2); q_m (mg/g) = D-R adsorption capacity; ε (kJ^{2}mol^{-2}) = the Polanyi potential is a constant related to adsorption energy; k_{RD} = a constant related to the mean sorption free energy E (kJ mol^{-1}) at the interphase. $E = \frac{1}{k_{RD}^{1/2}}$ $\varepsilon = RT\, Ln\, (1 + \frac{1}{C_e})$ R (kJmol^{-1}K^{-1}) the universal gas constant, T (Kelvin) is the temperature and C_e (mg/L) is as defined in Equation 1.
Redlich-Peterson (R-P) $q_e = \frac{k_R C_e}{1+ a_R C_e^{\beta}}$ Equation S9	q_e (mg/g) and C_e (mg/L) are similarly defined as in Equations (1-2); q_e (mg/g) is the amount of dye adsorbed at equilibrium; C_e (mg/L) is the concentration of adsorbate in solution at equilibrium; k_R (L/g) and a_R (L/mg) are constants while β has values between 0 to 1.
Sips $q_e = q_m \frac{(k_{LF} C_e)^{1/nLF}}{1+((k_{LF} C_e)^{1/nLF})}$ Equation S10	q_e (mg/g), q_m (mg/g), and C_e (mg/L) are similarly defined as in Equations (1-2); q_m is the maximum monolayer adsorption capacity; C_e (mg/L) is the concentration of adsorbate in solution at equilibrium; k_{LF} (L/mg) is the adsorption equilibrium constant; q_e (mg/g) = adsorption capacity at equilibrium; n_{LF} = non-linear dimensionless coefficient of the Sips model
Harkins-Jura (H-J): $q_e^{-2} = \frac{B}{A} - Log\, C_e^{1/A}$ Equation S11	The corresponding Harkins-Jura model terms are defined, as follows: q_e (mg/g) and C_e (mg/L) are similarly defined as in Equations (1-2); while A and B are the models constants which are related to the surface area of the adsorbent and nature of the adsorbate, respectively.

Table S2: Adsorption kinetic models and parameters

Models	Parameters
Pseudo first order (PFO) $q_t = q_e[1 - \exp(-k_1 t)]$ Equation S12 $ln(q_e - q_t) = lnq_e - k_1 t$ Equation S13	q_t and q_e (mg/g) are the quantities of pollutants adsorbed at time t and near dynamic equilibrium condition respectively; k_1 (min^{-1}) is the PFO rate constant. The *goodness-of-fit* to the kinetic results can reveal whether the PFO model provides support for a physisorption process for the heterogeneous system
Pseudo second order (PSO) $q_t = \dfrac{q_e^2(k_2 t)}{(1+q_e k_2 t)}$ Equation S14 $\dfrac{t}{q_t} = \dfrac{1}{k_2 q_e^2} + \dfrac{1}{q_e} t$ Equation S15	q_t (mg/g), q_e (mg/g) are defined as in Equations (12-13); and k_2 (g/mg.min) is the PSO rate constant.
Intra-particle diffusion (IPD) $q_t = k_p t^{1/2} + I$ Equation S16	q_t (mg/g) is the amount of adsorbed species at time t (min); k_p is IPD rate constant and I is related to boundary layer thickness.
Elovich $\dfrac{dq_t}{dt} = a\,e^{-bq_t}$ Equation S17	q_t (mg/g) is defined in Equation (18), a and b are the model constants, a (mg g^{-1} min^{-1}) is the initial adsorption rate while b relates to the extent of surface coverage and activation energy involved in chemisorption (m mg^{-1}).
Thomas $\dfrac{C_t}{C_o} = \dfrac{1}{1+exp\,(k_{Th}q_o m/v - k_{Th}C_o t)}$ Equation S18 $ln\left(\dfrac{C_o}{C_t} - 1\right) = \dfrac{k_{Th}q_o m_o}{q} - k_{Th}C_o t$ Equation S19	q_o is the Maximum adsorption capacity (mg/L); k_{Th} is the Thomas rate constant (mL/min.mg); C_o is the influent adsorbate concentration (mg/L); C_t is the effluent metal concentration (mg/L); m is the mass of adsorbent in the column (g); and v is the flow rate (mL/min).
Adams-Bohart $\dfrac{C_t}{C_o} = \exp\left(k_{AB}C_o t - k_{AB}N_o \dfrac{Z}{U}\right)$ Equation S20 $\ln\left(\dfrac{C_t}{C_o}\right) = k_{AB}C_o t - k_{AB}N_o \dfrac{Z}{U}$ Equation S21	C_o = influent adsorbate concentration (mg/L); C_t = effluent adsorbate concentration (mg/L) k_{AB} = rate constant of the model (L/mg.min); Z = bed height of column (cm); N_o = Maximum adsorption capacity (mg/L); U= linear velocity (cm/min), which can be related to the flow rate/column section area.
Bed Depth Service Time (BDST) $t = \dfrac{N_o}{FC_o}Z - \dfrac{1}{k_a C_o}\ln\left(\dfrac{C_o}{C_t} - 1\right)$ Equation S22	q_t and q_e (mg/g) are respectively the amount of pollutants adsorbed at time t and equilibrium time; k_2 (g/mg.min) is the PSO rate constant, k_a = rate constant of the BDST model (L/mg); Z = bed depth of column (cm); N_o = Maximum adsorption capacity (mg/L); F= linear velocity (cm/min) that relates to the flow rate/column section area; C_o = influent adsorbate

concentration (mg/L); and C_t is the effluent adsorbate concentration (mg/L).

Yoon-Nelson

$$\frac{C_t}{C_o} = \frac{1}{1+\exp{(k_{YN}\tau - k_{YN}t)}}$$ Equation S23

$$\ln\left(\frac{C_t}{C_o-C_t}\right) = k_{YN}t - \tau k_{YN}$$ Equation S24

C_o = influent adsorbate concentration (mg/L); C_t = effluent adsorbate concentration at time t (mg/L); k_{YN} = Yoon-Nelson rate constant (1/min); τ = time required for 50 % adsorbate breakthrough (min); and t = breakthrough time (min).