Studies on removal of As(III) and As(V) onto GAC/MnFe₂O₄ composite: isotherm studies and error analysis
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1. Isotherm studies

1.1. Single parameter model

1.1.1. Henry's law

Henry's law (Faust and Aly, 1987; Xue et al., 2001; Piccin et al., 2012) describes a suitable fit to the adsorption of adsorbate onto a uniform surface of adsorbent at adequately low adsorbate concentrations so that all adsorbate molecules are isolated from their closest neighbours. According to this isotherm, the liquid phase and adsorbed phase equilibrium adsorbate concentrations can be related in a linear equation. The Henry's law can be expressed as follows:

$$q_e = K_{HE} C_e \quad (1)$$

Higher the value of K_{HE} , stronger is the interaction between the adsorbate molecules and the adsorbent.

1.2. Two parameter model

1.2.1. Langmuir isotherm

Langmuir (Langmuir, 1918) has proposed an empirical model with an assumption that monolayer adsorption of adsorbate (the adsorbed film is basically a single molecule in thickness) takes place at a finite (limited) number of certain confined sites, without lateral interaction onto a structurally homogeneous adsorbent surface where all the adsorption sites are identical (Vijayaraghavan et al., 2006) and energetically same (i.e. constant heat of adsorption for all sites) (Kundu and Gupta, 2006). Langmuir has postulated that with the increase of distance, the intermolecular attractive forces rapidly decrease. At low adsorbate concentrations this model transforms to linear Henry's law, but it describes a constant monolayer adsorption capacity at high adsorbate concentrations. The Langmuir isotherm is expressed as follows:

$$q_s = \frac{q_{mL} K_L C_s}{1 + K_L C_s} \quad (2)$$

On the basis of the additional investigation of Langmuir isotherm, the dimensionless parameter of the equilibrium or separation factor or adsorption intensity (R_L) (Hall et al., 1966) can be expressed as follows:

$$R_L = \frac{1}{(1 + K_L C_0)} \quad (3)$$

The R_L parameter is measured as very consistent indicator of the adsorption. The isotherm profile can be inferred according to the value of R_L as Table S1.

1.2.2. Freundlich isotherm

The empirical Freundlich isotherm model (Freundlich, 1906) describes the non-ideal and reversible adsorption, not limited to the formation of monolayer such as Langmuir isotherm. The Freundlich isotherm defines the adsorption of adsorbate from solution to the surface of adsorbent and assumes that the stronger binding sites are initially employed and with the rise of degree of site occupation, the binding strength reduces. Thus, multilayer adsorption, with non-uniform distribution of adsorption heat and affinities onto the heterogeneous adsorbate surface without lateral interaction (Adamson and Gast, 1997), can be described by its relationship as follows:

$$q_s = K_F C_s^{\frac{1}{n_F}} \quad (4)$$

The value of n_F depends on the temperature and the given adsorbate-adsorbent interactions, including all factors influencing the adsorption process for instance adsorption intensity and adsorption capacity or surface homogeneity associated with the distribution of adsorption energy respectively. Though the Freundlich isotherm delivers ideas about the heterogeneity of surface as well as the exponential distribution of the active sites and their energies, it does not forecast any saturation of adsorbent surface by the adsorbate. Henceforth infinite surface coverage can be forecasted mathematically. The magnitude of $1/n_F$ ranges between 0 and 1, is an indicative of favourable adsorption, becoming more heterogeneous as its value tends to zero. Conversely the value of n_F of this isotherm, varying in the range of 1–10 directs favourable adsorption (Treybal, 1981). Higher value of n_F (smaller value of $1/n_F$) infers stronger interaction between adsorbate and adsorbent whereas $1/n_F$ equal to 1 specifies linear adsorption leading to indistinguishable adsorption energies for all sites (Delle Site, 2001).

The Freundlich model does not deliberate the adsorption saturation. In recent times, at vanishing concentrations, Freundlich isotherm is condemned due to its restriction of missing a fundamental thermodynamic basis and not reducing to the Henry's law. The magnitude of the exponent n_F indicates the adsorption favourability. Usually it is specified that value of n_F in the range 2–10 signifies worthy, 1–2 reasonably problematic in addition to less than 1 very poor adsorption characteristics (Shafique et al., 2012).

1.2.3. Temkin Isotherm

The isotherm studied by Temkin and Pyzhev (Temkin and Pyzhev, 1940) comprises a factor that covers the adsorbate–adsorbent interactions explicitly. By overseeing the exceptionally high and low concentrations of adsorbate, the model assumes that the heat of adsorption (function of temperature) of all molecules in the layer would reduce linearly rather than logarithmic with coverage owing to interactions between adsorbate and adsorbent. This isotherm assumes that the adsorption is regarded as a uniform distribution of binding energies up to some maximum energy. It is expressed as follows:

$$q_s = \frac{RT}{b_{TE}} \ln(K_{TE} C_s) = B_{TE} \ln(K_{TE} C_s) \quad (5)$$

1.2.4. Dubinin–Radushkevich isotherm

Dubinin (Dubinin and Radushkevich, 1947) has suggested a renowned model for the isotherms analysis of a high degree of regularity. Radushkevich (Radushkevich, 1949) and Dubinin (Dubinin, 1965) have stated that the typical adsorption curve is linked to the porous adsorbent structure. Dubinin–Radushkevich isotherm can be represented as follows (Polanyi, 1932):

$$q_s = q_{mDR} \exp \left\{ -K_{DR} \left[RT \ln \left(1 + \frac{1}{C_s} \right) \right]^2 \right\} = q_{mDR} \exp \left\{ -K_{DR} \varepsilon^2 \right\} \quad (6)$$

D–R isotherm narrates the energies heterogeneity adjacent to the surface of adsorbent. If a very trivial sub–region surface of the adsorption is selected and expected being almost by the Langmuir isotherm, the quantity $\sqrt{K_{DR}}$ can be connected to the mean adsorption energy, E , which is the free energy for transferring 1 mole of adsorbate from infinite distance in the aqueous phase to the adsorbent surface. The mean free energy (E ; KJ/mol) can be estimated as follows (Hobson, 1969):

$$E = \frac{1}{\sqrt{2K_{DR}}} \quad (7)$$

The magnitude of mean free energy of adsorption contributes information regarding adsorption mechanism, physical or chemical (Erdem et al., 2004). If the value of E varies between 8 and 16 KJ/mol, means that the adsorption process is nothing but ion–exchange

reaction (Kilislioğlu and Bilgin, 2003) and when E is less than 8 kJ/mol, it means that the physical adsorption process occurs (Lodeiro et al., 2006).

1.2.5. Activated sludge

Crombie–Quilty and McLoughin (Crombie–Quilty and McLoughin, 1983) have suggested an isotherm model describing formation of floc at an equilibrium concentration. Activated sludge model is exhibited as follows:

$$q_s = K_m \left(\frac{C_s}{M} \right)^{\frac{1}{N_m}} \quad (8)$$

Lower the value of K_m , lower is the possibility for tendency of floc formation. Lower the value of $1/N_m$ (less than 1) exhibits that any huge alteration in the equilibrium adsorbate concentration, would not affect an extraordinary alteration in the extent of formation of floc of adsorbate by adsorbent.

1.2.6. Jovanovic isotherm

Jovanovic (Jovanovic, 1969) has proposed a model taking the similar suppositions as that of Langmuir isotherm and moreover takes into account the surface binding vibrations of the adsorbed species. The Jovanovic isotherm signifies another approximation for monolayer localized adsorption without lateral interactions. This isotherm describes that the distribution of energy for Jovanovic local behaviour is a quasi–Gaussian function skewed in the trend of high adsorption energies. At high concentrations of adsorbate, it becomes the Langmuir isotherm, however does not follow the Henry's law. The Jovanovic model is expressed as follows:

$$q_s = q_{mJV} \{1 - \exp(-K_{JV} C_s)\} \quad (9)$$

1.3. Three parameter models

1.3.1. Redlich–Peterson isotherm

Redlich and Peterson (Redlich and Peterson, 1959) have comprised the characteristics of both Freundlich and Langmuir isotherms into one empirical equation including three parameters. It has a linear dependency onto concentrations of adsorbate in the numerator and an exponential function in the denominator (Ng et al., 2002) for signifying the adsorption equilibrium over an extensive range of concentrations, which is successfully applicable either in homogeneous or heterogeneous systems because of its flexibility (Gimbert et al., 2008). The adsorption mechanism is hybrid and does not obey adsorption of ideal monolayer. At high concentration, this isotherm converts to Freundlich isotherm model but it approaches Henry's law at low concentration. Redlich–Peterson isotherm is given as follows:

$$q_s = \frac{K_{RP} C_s}{1 + \alpha_{RP} C_s^{\beta_{RP}}} \quad (10)$$

The exponent, β_{RP} , generally ranges between 0 and 1. While β_{RP} is equal to 1 this isotherm approaches Langmuir isotherm and β_{RP} is equal to 0 this isotherm approaches to Freundlich isotherm (Jossens et al., 1978).

1.3.2. Sips isotherm

Sips model (Sips, 1948) is a hybrid form of both Freundlich and Langmuir isotherms inferred to forecast the heterogeneous adsorption systems (Gunay et al., 2007) and avoid the restriction to increase adsorbate concentrations accompanying with Freundlich isotherm model. It efficiently approaches to Freundlich isotherm at low adsorbate concentrations and does not follow Henry's law. It forecasts a monolayer adsorption capacity characteristic of the Langmuir isotherm at high adsorbate concentrations. Sips isotherm is defined as follows:

$$q_s = \frac{K_S q_{mS} C_s^{\frac{1}{m_S}}}{1 + K_S C_s^{\frac{1}{m_S}}} \quad (11)$$

When m_S equal to 1 this isotherm approaches Langmuir isotherm and m_S equal to 0 this isotherm approaches Freundlich isotherm. As a universal rule, the equation parameters are ruled primarily by the operating parameters for example the change in concentration, temperature and pH (Pérez–Marín et al., 2007).

1.3.3. Toth isotherm

Toth has established an empirical equation is from potential theory (Toth, 1971) for refining the fitting of Langmuir isotherm (experimental results) and necessary to describe heterogeneous adsorption systems which can fulfil high as well as low adsorbate concentration (Vijayaraghavan et al., 2006). This isotherm assumes asymmetrical distribution of quasi–Gaussian energy, with utmost of the active sites having adsorption energy lesser than the mean or maximum (peak) value (Ho et al., 2002). Toth isotherm is presented as follows:

$$q_s = \frac{q_{mT} K_T C_s}{(1 + (K_T C_s)^{n_T})^{\frac{1}{n_T}}} \quad (12)$$

If n_T is equal to 1, this recommends that the process happens onto a homogenous surface, this isotherm approaches to Langmuir isotherm.

1.3.4. Brouers–Sotolongo isotherm

Brouers et al. (Brouers et al., 2005) has formulated an isotherm in the form of deformed exponential (Weibull) function for adsorption onto the heterogeneous surface mainly because of Langmuir who has recommended the extension of the simple Langmuir

isotherm to non-uniform adsorbent surfaces. He has assumed that the surface of adsorbent consists of a fixed number of patches of active sites of equal energy. Brouers–Sotolongo model is represented as follows:

$$q_s = q_{mBS}(1 - \exp(-K_{BS}C_s^\alpha)) \quad (13)$$

The parameter α is related with distribution of adsorption energy and the energy of heterogeneity of the adsorbent surfaces at the given temperature (Ncibi et al., 2008).

1.3.5. Vieth–Sladek isotherm

Vieth and Sladek (Vieth and Sladek, 1965) have proposed a model throughout the process of framing a different method for evaluating diffusion rates in solid adsorbents from transient adsorption. This isotherm has the distinct two sections: one defined by a linear section (Henry's law) and remaining generally detected non-linear section (Langmuir isotherm). The linear section clarifies the physisorption of gas molecules onto the amorphous adsorbent surfaces and the non-linear section explains the adherence of gas molecules to sites on the porous adsorbent surfaces. Vieth–Sladek isotherm is expressed as follows:

$$q_s = K_{VS}C_s + \frac{q_{mVS}\beta_{VS}C_s}{1 + \beta_{VS}C_s} \quad (14)$$

1.3.6. Koble–Corrigan isotherm

Koble and Corrigan (Koble and Corrigan, 1952) have proposed a three-parameter isotherm model, which is a combination of both Freundlich and Langmuir isotherm models to indicate the equilibrium adsorption data. This isotherm has resemblance to the Sips isotherm. Koble–Corrigan isotherm can be represented as follows:

$$q_s = \frac{A_{KC}B_{KC}C_s^{n_{KC}}}{1 + B_{KC}C_s^{n_{KC}}} \quad (15)$$

At high adsorbate concentrations, Koble–Corrigan model reduces to a Freundlich isotherm that reaches the highest adsorption, and this isotherm is valid while n_{KC} is greater than or equal to 1 (Hamidpour et al., 2010). The constant n_{KC} is less than 1, signifies that the model is incapable to define the experimental data in spite of the high value of correlation coefficient or low error value (Abdelwahab, 2007).

1.3.7. Khan isotherm

Khan et al. (Khan et al., 1997) has postulated a general model for adsorption of bi-adsorbate from dilute aqueous solutions. This isotherm has typical features for example applicable in both limits Freundlich on one end and Langmuir isotherm on the other end. The general model for a single adsorbate, Khan isotherm is expressed as follows:

$$q_s = \frac{q_{mK}b_KC_s}{(1+b_KC_s)^{a_K}} \quad (16)$$

While a_K is equal to 1, above equation approaches the Langmuir isotherm and at higher values of concentration, this model reduces to the Freundlich isotherm.

1.3.8. Hill isotherm

Hill (Hill, 1910) has proposed an isotherm model from the non-ideal competitive adsorption model (Koopal et al., 1994) to define different adsorbate binding on a homogeneous surface of adsorbent. This isotherm model undertakes that the adsorption is basically a cooperative manifestation, including the ligand binding capability at one site onto the macromolecule, influencing various binding sites onto the same macromolecule (Ringot et al., 2007). The Hill isotherm can be represented as follows:

$$q_s = \frac{q_{mH} C_s^{n_H}}{K_H + C_s^{n_H}} \quad (17)$$

If n_H is greater than 1, this isotherm indicates positive cooperativity in binding, n_H is equal to 1, it indicates non-cooperative or hyperbolic binding and n_H is less than 1, indicating negative cooperativity in binding.

1.3.9. Jossens isotherm

Jossens (Jossens et al., 1978) has predicted a simple equation based on the energy distribution of adsorbate-adsorbent interactions onto adsorption sites. It assumes the heterogeneous adsorbent surface, regarding the interactions which it involves with the adsorbate. Jossens isotherm (Hadi et al., 2012) can be represented as follows:

$$q_s = \frac{K_J C_s}{1 + J C_s^{b_J}} \quad (18)$$

At low capacities this isotherm reduces to Henry's law.

1.3.10. Fritz-Schlunder-III isotherm

Fritz and Schlunder have proposed an empirical expression (Fritz and Schlunder, 1974) which can fit over an extensive range of experimental results because of huge number of coefficients in their isotherm. Fritz-Schlunder-III isotherm can be expressed as follows:

$$q_s = \frac{q_{mFS} K_{FS} C_s}{1 + K_{FS} C_s^{n_{FS}}} \quad (19)$$

If n_{FS} is equal to 1, the Fritz-Schlunder-III model becomes the Langmuir model but for high concentrations of adsorbate, the Fritz-Schlunder-III reduces to the Freundlich model.

1.3.11. Unilan isotherm

Valenzuela and Myers have proposed another empirical relationship which has been recommended for the equilibrium data analysis by Unilan, having three isotherm parameters.

It is frequently used for adsorption of gas phase onto a heterogeneous adsorbent surface (Valenzuela and Myers, 1989). This empirical equation supposes the application of the local Langmuir isotherm and uniform energy distribution. This equation is restricted to Henry's law, thus it is valid at extremely low adsorbate concentrations (Quinone and Guiochon, 1996). Unilan isotherm (Chern and Wu, 2001; Hadi et al., 2012) is depicted as follows:

$$q_s = \frac{q_{mU}}{2s} \ln \left\{ \frac{1 + K_U C_s \exp(s)}{1 + K_U C_s \exp(-s)} \right\} \quad (20)$$

The higher the model exponent s , the system is more heterogeneous. If s is equal to 0, the Unilan isotherm model becomes the classical Langmuir model as the range of energy distribution is zero in this limit (Quinone and Guiochon, 1996).

1.3.12. Holl–Krich isotherm

Parker (Parker, 1995) has proposed a modified form of Langmuir isotherm, Holl–Krich type. This isotherm (Khan et al., 1997) is represented as follows:

$$q_s = \frac{q_{mHK} K_{HK} C_s^{n_{HK}}}{1 + K_{HK} C_s^{n_{HK}}} \quad (21)$$

The Holl–Krich isotherm becomes the Freundlich isotherm at low concentrations. The capacity reaches a finite capacity more leisurely than the Langmuir isotherm at high concentrations.

1.3.13. Langmuir–Freundlich isotherm

Langmuir–Freundlich isotherm (Sips, 1948) includes the knowledge of adsorption onto heterogeneous surfaces and describes the distribution of adsorption energy onto this heterogeneous surface of adsorbent. It effectively becomes the Freundlich isotherm at low adsorbate concentrations and therefore does not follow Henry's law. It forecasts a monolayer adsorption capacity at high adsorbate concentrations, characteristic of the Langmuir isotherm. Langmuir–Freundlich isotherm (Hamdaoui et al., 2000; Hadi et al., 2012) can be expressed as follows:

$$q_s = \frac{q_{mLF} (K_{LF} C_s)^{m_{LF}}}{1 + (K_{LF} C_s)^{m_{LF}}} \quad (22)$$

The model becomes Langmuir isotherm in case of homogeneous surfaces. In this isotherm the model exponent the value of m_{LF} is between 0 and 1. This parameter increases with decreasing degree of surface heterogeneity. For m_{LF} is equal to 1, this model covert to Langmuir model.

1.3.14. Langmuir–Jovanovic isotherm

Shahbeig (Shahbeig et al., 2013) has proposed an empirical relation which is the combined form of both Langmuir and Jovanovic isotherm. The Langmuir–Jovanovic model is presented as follows:

$$q_s = \frac{q_{mLJ} C_s \{1 - \exp(-K_{LJ} C_s^{n_{LJ}})\}}{1 + C_s} \quad (23)$$

1.3.15. Jovanovic–Freundlich isotherm

The Jovanovic–Freundlich model (Quin˜ones and Guiochon, 1996) has been derived to define adsorption equilibrium of single adsorbate onto heterogeneous adsorbent surfaces from a differential relationship connecting the surface coverage and the bulk concentrations of adsorbate. While the surface turns into homogeneous, this isotherm becomes Jovanovic isotherm. At high concentration, it becomes the Langmuir isotherm but at low concentrations it becomes the Freundlich isotherm and does not follow the Henry's law. The energy distribution analogous to this isotherm for Jovanovic local behaviour is basically a quassi–Guassian function skewed in the way of high adsorption energies at low concentrations. Jovanovic–Freundlich isotherm (Markovski et al., 2014) can be represented as follows:

$$q_s = q_{mJF} (1 - \exp\{(-K_{JF} C_s)^{n_{JF}}\}) \quad (24)$$

1.3.16. Radke–Prausnitz isotherm

Radke and Prausnitz (Radke and Prausnitz, 1972) have proposed an empirical relationship owing to the concepts of thermodynamic ideal solution for dilute solutions observed suitable for heterogeneous equilibrium studies. This isotherm suggests a minor alteration to the Langmuir isotherm by incorporating a coefficient for developing the experimental data fitting. The isotherm approaches Henry's law at low concentrations, but the equilibrium adsorption capacity inclines to infinity similar to Freundlich isotherm at high concentrations. The Radke–Prausnitz isotherm model (Hamdaoui and Naffrechoux, 2007; Hadi et al., 2012) can be represented as follows:

$$q_s = \frac{q_{mRPI} K_{RPI} C_s}{(1 + K_{RPI} C_s)^{m_{RPI}}} \quad (25)$$

$$q_s = \frac{q_{mRPII} K_{RPII} C_s}{1 + K_{RPII} C_s^{m_{RPII}}} \quad (26)$$

$$q_s = \frac{q_{mRPIII} K_{RPIII} C_s^{m_{RPIII}}}{1 + K_{RPIII} C_s^{m_{RPIII}-1}} \quad (27)$$

If the value of both m_{RPI} and m_{RPII} is equal to 1, the Radke–Prausnitz I, II models reduce to the Langmuir model but at low concentrations, the models become Henry's law; but for high adsorbate concentration, the Radke–Prausnitz I and II models become the

Freundlich model. But the Radke–Prausnitz–III equation reduces to Henry's law while the exponent m_{RPIII} is equal to 1 and become Langmuir isotherm when the exponent m_{RPIII} is equal to 0.

1.3.17. Langmuir–Freundlich–Jovanovic isotherm

The equilibrium adsorption isotherm is the utmost vital part of the current investigation for exploring the adsorption mechanism. Key adsorption properties like the adsorption affinity and the surface property of adsorbent and the maximum adsorption capacity can be calculated from the adsorption isotherm and correlative constants. In the present investigation, an innovative and modified model has been derived to correlate equilibrium adsorption data. A combination of Langmuir–Freundlich and Jovanovic models were used with the aim of forming a new isotherm model with less error compared to that of other models. Subsequently, the resulting model can be expressed as follows:

$$q_e = \frac{q_{mLFJ} C_e^{n_{LFJ}} \{1 - \exp(-(K_{LFJ} C_e)^{n_{LFJ}})\}}{1 + C_e^{n_{LFJ}}} \quad (28)$$

1.4. Four parameter model

1.4.1. Marczewski–Jaroniec Isotherm

Marczewski–Jaroniec isotherm (Parker, 1995) which is as well recognized as the four-parameter general Langmuir equation is recommended on the basis of the suppositions of local Langmuir isotherm and the adsorption energies distribution in the active sites. Marczewski–Jaroniec isotherm (Sivarajasekar and Baskar, 2013) is expressed as follows:

$$q_e = q_{mMJ} \left(\frac{(K_{MJ} C_e)^{n_{MJ}}}{1 + (K_{MJ} C_e)^{n_{MJ}}} \right)^{\frac{m_{MJ}}{n_{MJ}}} \quad (29)$$

The parameter n_{MJ} and m_{MJ} , characterize the heterogeneity of surface, can vary from 0 to 1. This isotherm reduces to Langmuir isotherm for the value of both n_{MJ} and m_{MJ} equal to 1, to Langmuir–Freundlich isotherm for n_{MJ} equal to m_{MJ} connected with the symmetrical quasi–Gaussian energy distribution and to the Toth isotherm for m_{MJ} equal to 1 corresponding to asymmetrical quasi–Gaussian energy distribution. The parameter m_{MJ} describes the spreading of the distribution in the path of higher adsorption energies, while n_{MJ} describes this spreading in the path of lesser adsorption energies.

1.4.2. Baudu isotherm

Baudu (Baudu, 1990) has evaluated the Langmuir coefficients, K_L and q_{mL} , measuring tangents at different equilibrium concentrations and he has derived that they are not constants

over a wide range of concentration. Thus the Langmuir equation has been reduced to the Baudu equation (Hamdaoui and Naffrechoux, 2007) as follows:

$$q_s = \frac{q_{mB} b_B C_s^{(1+x+y)}}{1 + b_B C_s^{(1+x)}} \quad (30)$$

This model is only applicable in the range of $(1 + x + y) < 1$ and $(1 + x) < 1$.

For lower surface coverage, Eq. (36) becomes the Freundlich equation, i.e.:

$$q_s = \frac{q_{mB} b_B C_s^{(1+x+y)}}{1 + b_B C_s} \quad (31)$$

1.4.3. Fritz–Schlunder–IV isotherm

Fritz and Schlunder (Fritz and Schlunder, 1974) have postulated another four-parameter empirical model including the characteristics of both Langmuir and Freundlich isotherms. This isotherm (Hamdaoui and Naffrechoux, 2007) is given as follows:

$$q_s = \frac{A_{FS} C_s^{a_{FS}}}{1 + B_{FS} C_s^{b_{FS}}} \quad (32)$$

These isotherm is valid when the values of a_{FS} and b_{FS} are less than or equal to 1. At high adsorbate concentration, Fritz–Schlunder–IV isotherm becomes Freundlich equation. Conversely for the value of both a_{FS} and b_{FS} equal to 1, this isotherm reduces to Langmuir isotherm, where K_L is equal to b_{FS} is the Langmuir adsorption constant (L/mg) linked with the energy of adsorption and A_E is equal to $K_L q_{mL}$.

At high concentrations of the adsorbate in the liquid-phase, Eq. (38) becomes the Freundlich equation, i.e.:

$$q_s = \frac{A_{FS}}{B_{FS}} C_s^{a_{FS} - b_{FS}} \quad (33)$$

where A_{FS}/B_{FS} and $(a_{FS} - b_{FS})$ represent, the parameters K_F and $1/n_F$ of the Freundlich model respectively.

1.5. Five parameter model

1.5.1. Fritz–Schlunder–V isotherm

Fritz and Schlunder (Fritz and Schlunder, 1974) have developed a five-parameter empirical model including more number of constants. The increased number of constants would be capable for simulating the model variations more precisely and this model which can be used over a wide range of equilibrium data. The Fritz–Schlunder–V isotherm (Hamdaoui and Naffrechoux, 2007) is expressed as follows:

$$q_s = \frac{q_{mFS} K_1 C_s^{a_{FS}}}{1 + K_2 C_s^{b_{FS}}} \quad (34)$$

This isotherm is valid only in the range of α_{FS} value less than or equal to 1 and β_{FS} value less than or equal to 1. The five-parameter Fritz–Schlunder–V model approaches Langmuir model while the values of both the exponents α_{FS} and β_{FS} is equal to 1 and for higher adsorbate concentrations, it reduces to the Freundlich model.

2. Determining adsorption isotherm parameters by non-linear regression

2.1. Residual Sum of Squares Error (SSE)

$$SSE = \sum_{i=1}^n (q_{s,model} - q_{s,exp})_i^2 \quad (35)$$

A value near to 0 specifies that the model has a lesser random error component and the fit will be more suitable for forecasting (Tsai and Juang, 2000; Dixit et al., 2011; Soares et al., 2014).

2.2. Reduced Chi square (Reduced χ^2)

$$Reduced \chi^2 = \frac{1}{(n-p)} \sum_{i=1}^n (q_{s,model} - q_{s,exp})_i^2 \quad (36)$$

The value of Reduced χ^2 will be a smaller number, if the model predicted data are almost analogous to the experimental data, but if they differ; reduced χ^2 will be a bigger number (Ho et al., 2005; Galindo et al., 2013).

2.3. Coefficient of determination (R^2)

$$R^2 = 1 - \frac{\sum_{i=1}^n (q_{s,model} - q_{s,exp})_i^2}{\sum_{i=1}^n (q_{s,exp} - \bar{q}_{s,exp})_i^2} \quad (37)$$

The value of R^2 can be in the range of 0 and 1. With a value closer to 1 signifies that a larger percentage of variance is accounted for by the model (Dixit et al., 2011; Hossain et al., 2012; Soares et al., 2014).

2.4. Adjusted R-square ($\bar{R}^2$)

$$\bar{R}^2 = 1 - \frac{\sum_{i=1}^n (q_{s,model} - q_{s,exp})_i^2 / (n-p)}{\sum_{i=1}^n (q_{s,exp} - \bar{q}_{s,exp})_i^2 / (n-1)} \quad (38)$$

The value of $\bar{R}^2$ can also vary between 0 and 1, with a value near to 1 indicating the more suitable fit for model prediction (Soares et al., 2014).

2.5 Correlation coefficient (R value)

$$R = \sqrt{1 - \frac{\sum_{i=1}^n (q_{s,model} - q_{s,exp})_i^2}{\sum_{i=1}^n (q_{s,exp} - \bar{q}_{s,exp})_i^2}} \quad (39)$$

R value lies between 0 and 1. A value is nearer to 1 suggests the better curve fitting (Bates and Watts, 1988; Ratkowsky, 1990; Seber and Wild, 2003).

2.6. Root mean square of the error or the Standard Deviation (Root–MSE)

$$Root\ MSE = \sqrt{\frac{1}{(n-p)} \sum_{i=1}^n (q_{s,model} - q_{s,exp})^2} \quad (40)$$

The smaller Root–MSE value indicates the better curve fitting (Tsai and Juang, 2000; Padmesh et al., 2006).

Table S1: Nature of the isotherm for different values of R_L

R_L value	Type of isotherm
$R_L > 1$	Unfavourable adsorption
$R_L = 1$	Linear
$R_L = 0$	Irreversible
$0 < R_L < 1$	Favourable

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