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Isotherm investigation for the sorption of fluoride onto Bio-F: comparison of linear and non-linear regression method

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Abstract A comparison of the linear and non-linear regression method in selecting the optimum isotherm among three most commonly used adsorption isotherms (Langmuir, Freundlich, and Redlich–Peterson) was made to the experimental data of fluoride (F) sorption onto Bio-F at a solution temperature of 30 ± 1 °C. The coefficient of correlation (r^2) was used to select the best theoretical isotherm among the investigated ones. A total of four Langmuir linear equations were discussed and out of which linear form of most popular Langmuir-1 and Langmuir-2 showed the higher coefficient of determination (0.976 and 0.989) as compared to other Langmuir linear equations. Freundlich and Redlich–Peterson isotherms showed a better fit to the experimental data in linear least-square method, while in non-linear method Redlich–Peterson isotherm equations showed the best fit to the tested data set. The present study showed that the non-linear method could be a better way to obtain the isotherm parameters and represent the most suitable isotherm. Redlich–Peterson isotherm was found to be the best representative ($r^2 = 0.999$) for this sorption system. It is also observed that the values of β are not close to unity, which means the isotherms are approaching the Freundlich but not the Langmuir isotherm.

Abbreviations

F	Fluoride
Bio-F	Bio-filter
r^2	Coefficient of correlation
NaF	Sodium fluoride
mg	Milligramme
g/L	Gramme per litre
mg/L	Milligramme per litre
°C	Degree centigrade
HDPE	High-density polyethylene
K_L	Adsorption equilibrium constant
Q_m	Maximum adsorption capacity
q_e	Adsorbate adsorbed onto adsorbent
C_e	Equilibrium liquid-phase concentration
K_F	Freundlich constant
$1/n$	Heterogeneity factor
K_R	Redlich–Peterson constant
a_R	Redlich–Peterson constant
β	Redlich–Peterson constant
q_m	Equilibrium capacity

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Introduction

Among the various methods used for defluoridation of drinking water, the adsorption process has been widely used because of its simplicity, affordability, easy operation, and satisfactory results (Liu et al. 2010; Deng et al. 2011; Bhatnagar et al. 2011; Xiang et al. 2014). Adsorption process includes the selective transfer of solute

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components onto the surface or the bulk of solid adsorbent materials in the aqueous phase (Kumar and Sivanesan 2007). The effectiveness of an adsorbent is estimated on the basis of its uptake capacity, adsorption rate, mechanical strength, possibility of regeneration, and reuse options (Tang and Zhang 2016). Among these, adsorbent capacity is the most important parameter which plays a vital role in overall process of adsorption (Oh and Park 2002; Gong et al. 2005). The uptake capacity and adsorption performance are usually determined on the basis of equilibrium experiments and sorption isotherms describing the interaction of pollutant with the adsorbent material (Brdar et al. 2012). The equilibrium studies are also very important in optimizing the design parameters for any adsorption system which provide sufficient information about physicochemical data to evaluate the adsorption process as a unit operation (Leyva-Ramos et al. 2010). The distribution of a solute between solid adsorbent and liquid phase is also a measure of the position of equilibrium. Therefore, equilibrium data should be accurately fit into different isotherm models to find a suitable one that can be used to design the process (Khaled et al. 2009).

Among the various tested isotherms for the defluoridation of drinking water, Langmuir, Freundlich, and Redlich–Peterson isotherms are frequently used over a wide concentration range of solute and sorbent to describe the adsorption equilibrium for water and wastewater treatment applications (Ho et al. 2005; Ho 2006a, b; Kumar and Sivanesan 2007).

The conventional approach for parameter evaluation of non-linear forms of aforementioned isotherms involves linearization of the expressions through transformation, followed by the linear regression method. The main disadvantage of the linear regression technique, that limit its use, includes estimation of only two variables in an empirical equation; whereas, non-linear optimization provides a more complex, yet mathematically rigorous method to determine the isotherm parameter values (Pal et al. 2013).

Linear regression analysis has been frequently employed in accessing the quality of fits and adsorption performance for fluoride removal from aqueous solutions (Fan et al. 2003; Onyango et al. 2004; Kamble et al. 2009; Foo and Hameed 2010). The fitting validity of different models was tested in linearized forms using coefficient of determination. Some other methods, recently were reported to predict the optimum isotherm, which includes correlation coefficient, the sum of errors squared, a hybrid error function, Spearman's correlation coefficient, Standard deviation of relative errors, coefficient of non-determination Marquardt's percent standard deviation, the average relative error, and the sum of absolute errors (Kumar et al. 2008; Foo and Hameed 2010). Currently, non-linear regression

method is observed to be the best way in selecting the optimum isotherm, but very limited published literature is available for such type of adsorption systems, i.e., Bio-F–F system. This method of non-linear regression involves the step of minimizing the error distribution between the experimental equilibrium data and predicted isotherm (Krishni et al. 2014).

Having these considerations in mind, a comparison of linear least squares method and non-linear regression method was discussed in present study using the experimental adsorption data of F onto Bio-F. The three widely used isotherms (Langmuir, Freundlich, and Redlich–Peterson) were investigated to discuss this issue. A trial-and-error optimization method was used for the non-linear regression using the solver add-in function, Microsoft Excel, Microsoft Corporation (Kumar and Sivanesan 2007; Krishni et al. 2014). In order to solve the non-linear equations of applied isotherms, an efficient Microsoft's add-in software *xlstat* is used in this study (Shahmohammadi-Kalalagh and Babazadeh 2014; Kausar et al. 2014). This study was done in continuation of our previous work (Yadav et al. 2014, 2015) to examine the most suitable isotherm for Bio-F and F system using linear and non-linear equations.

Experimental programmes

Materials and methods

All chemicals used throughout this study were of analytical grade and purchased mainly from Merck India Limited. The stock solution of fluoride was prepared by dissolving the appropriate amount (221 mg) of anhydrous NaF in 1 L of double-distilled water to a concentration of 100 mg/L. The test working solutions of F were prepared by successive dilution with double-distilled water. All the batch adsorption studies were undertaken using Bio-F adsorbent, manufactured by HES Water Engineers (I) Pvt. Ltd. (a joint venture company of water engineers, Australia). More details about this adsorbent are given in our previous studies (Yadav et al. 2014, 2015).

Batch equilibrium adsorption experiments were conducted to investigate the adsorption behaviour of Bio-F at a constant dose of 10 g/L and varying concentrations of fluoride. All the adsorption experiments were carried out at room temperature of 30 ± 1 °C. To study the various process parameters, a series of conical flasks having test solution and adsorbent, was then shaken at a constant speed of 90 rpm in an orbital shaker with thermostatic control (Remi, India). At the end of the required contact time (when equilibrium was achieved), flasks were removed from the shaker and allowed to stand for 5 min for the

Table 1 Selected adsorption isotherms and their linear forms with corresponding plots

Isotherm model (non-linear form)		Linear form	Plot
Langmuir 1	$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e}$	$C_e/q_e = \frac{1}{q_m} C_e + \frac{1}{K_L q_m}$	C_e/q_e vs C_e
Langmuir 2		$\frac{1}{q_e} = \left(\frac{1}{K_L q_m}\right)\frac{1}{C_e} + \frac{1}{q_m}$	$\frac{1}{q_e}$ vs $\frac{1}{C_e}$
Langmuir 3		$q_e = q_m - \left(\frac{1}{K_L}\right)\frac{q_e}{C_e}$	q_e vs $\frac{q_e}{C_e}$
Langmuir 4		$\frac{q_e}{C_e} = K_L q_m - K_L q_e$	$\frac{q_e}{C_e}$ vs q_e
Freundlich	$q_e = K_F C_e^{1/n}$	$\log q_e = \log K_F + \frac{1}{n}\log C_e$	$\log q_e$ vs $\log C_e$
Redlich–Peterson	$q_e = \frac{K_R C_e}{1 + a_R C_e^{\beta}}$	$\ln\left(K_R \frac{C_e}{q_e} - 1\right) = \beta\ln(C_e) + \ln(a_R)$	$\ln\left(K_R \frac{C_e}{q_e} - 1\right)$ vs $\ln(C_e)$

K_L is the adsorption equilibrium constant (L/mg), K_F and $1/n$ are empirical constants of Freundlich isotherm, K_R, a_R and β ($0 < \beta < 1$) are three constants of Redlich–Peterson Isotherm

adsorbent to settle down. After the fluoride adsorption equilibrium studies, the treated and untreated samples were filtered through Whatman filter paper No. 42 and stored in HDPE bottles for the further analysis of the residual F using an ion meter (Thermo Scientific Orion 5-Star ion meter).

Isotherm models

Equilibrium isotherm equations are used in this study to describe the experimental sorption data of present adsorption system. The equation parameters with the underlying thermodynamic assumptions of these isotherm models often provide an insight into the sorption mechanisms, surface properties, as well as the degree of affinity of the sorbents (Ho 2006a, b). The three most common isotherms for describing solid–liquid sorption systems are Langmuir, Freundlich, and Redlich–Peterson isotherms. Langmuir adsorption isotherm, which was originally developed to describe gas–solid phase adsorption onto activated carbon, has been traditionally used to investigate the performance and potential of different bio-sorbents (Foo and Hameed 2010). This is also valid for adsorption of solutes from aqueous solutions, as monolayer adsorption on specific homogenous sites (a finite number of identical sites) within the adsorbent surface. Therefore, the Langmuir isotherm model estimates the maximum adsorption capacity achieved from complete monolayer coverage on the adsorbent surface (Nur et al. 2014). The Freundlich isotherm is an empirical model, which is the earliest known relationship describing the adsorption process. It is applicable to the gas–solid phase non-ideal and multilayer adsorption on heterogeneous surfaces with interaction between adsorbed molecules. It also suggests that sorption energy exponentially decreases upon the completion of adsorption process. Therefore, Freundlich isotherm can be applied to describe the heterogeneous adsorption systems

(Ghorai and Pant 2005). The Redlich–Peterson isotherm, which contains three parameters, K_R, a_R and β, also includes the features of Langmuir and Freundlich isotherm (Brdar et al. 2012; Khaled et al. 2009). This model has a linear dependence on concentration in the numerator and an exponential function in the denominator to describe adsorption equilibrium over a wide concentration range of adsorbate, thus can be applied for both homogeneous or heterogeneous systems due to its versatility (Foo and Hameed 2010). The non-linear and linear forms of equation of Langmuir, Freundlich, and Redlich–Peterson isotherms are given in Table 1.

Results and discussion

A trial-and-error procedure was applied to determine the parameters of the investigated isotherms. In this study, the coefficient of determination, r^2, was used for the experimental data to determine the best-fit isotherm model out of the three used isotherms (Freundlich, Langmuir and Redlich–Peterson). The value of r^2 for non-linear regression was evaluated using following formula (Ho 2006a, b):

$$r^2 = \frac{\sum(q_m - \overline{q_e})^2}{\sum(q_m - \overline{q_e})^2 - \sum(q_m - q_e)^2},$$

where q_m is the sorption equilibrium capacity obtained by calculating from the isotherm model, q_e is experimental capacity obtained from experiment, and $\overline{q_e}$ is the average of q_e values.

Linear regression method

Linear regression is the most commonly used method to determine the best-fit isotherm and the method of least squares has been used for finding parameters of the
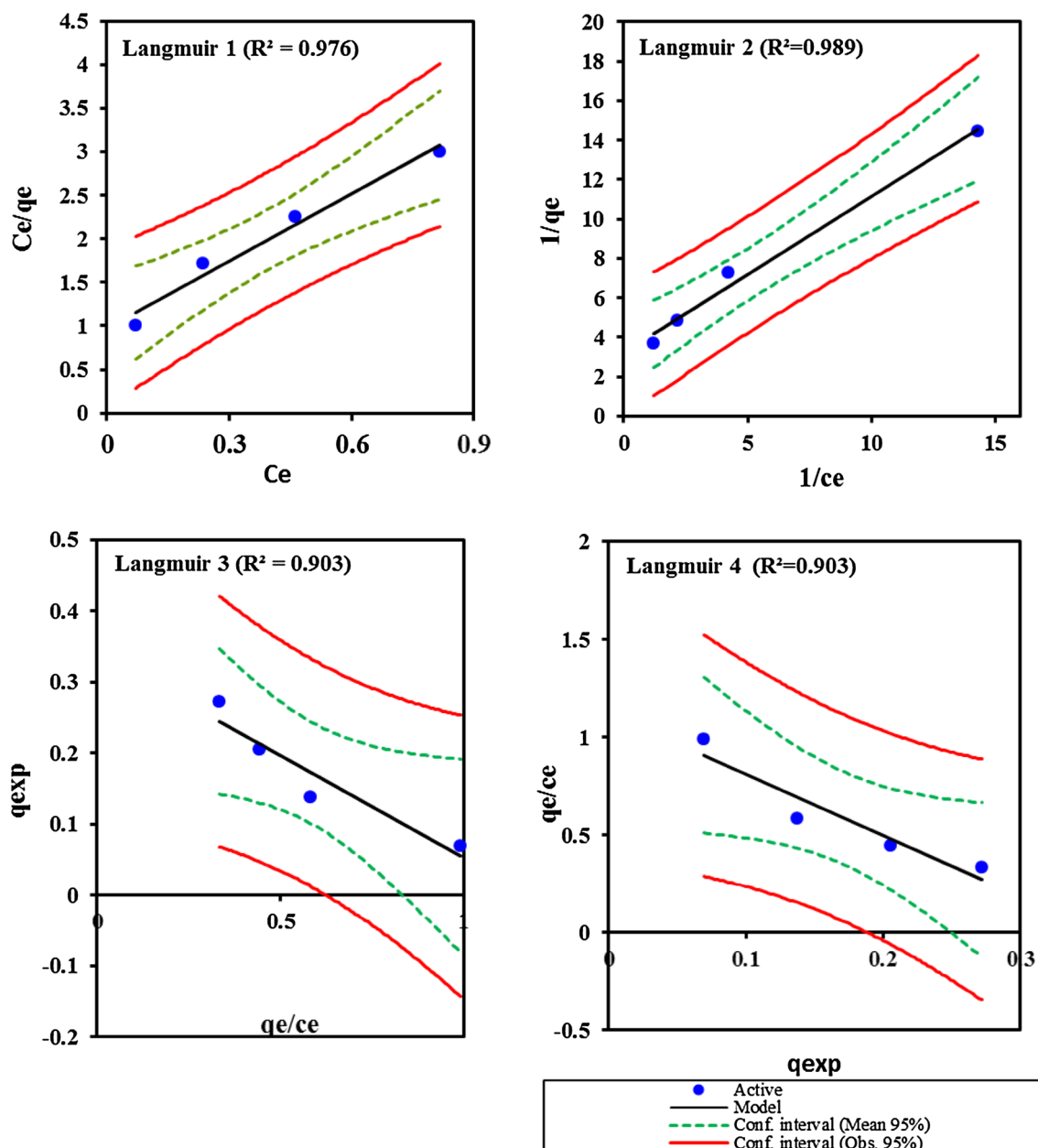
Fig. 1 Different linear forms of Langmuir isotherm obtained using the linear method for the sorption of fluoride onto Bio-F

isotherm models (Krishni et al. 2014; Kausar et al. 2014). It was observed that Langmuir isotherm could be linearized into at least four different forms as in Table 1, and simple linear regression will result in different parameter estimates. The most popular linear forms used are Langmuir-1 and Langmuir-2. The best-fit is obtained using Langmuir-2 because of the minimized deviations from the fitted equation resulting in the best error distribution (Ho 2006a, b). Figure 1 shows the plots of four linear Langmuir equations and the experimental data for the sorption of F onto Bio-F, and it was found that Langmuir-2 isotherm provides a better fit to the experimental equilibrium data.

The applicability of the Freundlich isotherm model was also analysed, using the same set of experimental data, by plotting $\log q_e$ vs $\log C_e$. Considering the linear forms of Langmuir isotherm for the comparison between the different isotherms, Freundlich isotherm was found to be more suitable as compared to all linear forms of the Langmuir isotherm because of the higher value of coefficient of determination, r^2. The Freundlich isotherm constants, K_F, $1/n$, and coefficients of determination are calculated and shown in Table 2.

Figure 2 shows the plots of linear Freundlich equations with experimental data for sorption of F onto Bio-F. The

Table 2 Isotherm parameters obtained using the linear and non-linear method

	Langmuir isotherm			Freundlich isotherm			Redlich–Peterson isotherm			
	Q_m	K_L	R^2	K_F	n	R^2	K_R	a_R	β	R^2
Linear 1	0.39	2.7	0.976	0.31	1.79	0.999	18.8	59.94	0.45	0.999
Linear 2	0.31	4.01	0.989							
Linear 3	0.34	3.48	0.903							
Linear 4	0.36	3.14	0.903							
Non-linear	0.531	0.246	0.969	0.631	1.697	0.969	20.12	64.77	0.464	0.999

Redlich–Peterson isotherm constants, K_R, a_R and β, as well as the r^2 for present adsorption system were obtained using the linear form of isotherm and presented in Table 2.

In all cases the Redlich–Peterson isotherm exhibited the highest coefficient of determinations same as Freundlich isotherm, which provided a considerably better fit as compared to Langmuir but similar to the Freundlich isotherm. It can also be observed that the values of β are not close to unity, which means the isotherms are approaching the Freundlich and not the Langmuir. Figure 3 shows the

plot of the Redlich–Peterson isotherm equations with the equilibrium experimental data.

Non-linear regression method

Non-linear regression method is a trial-and-error procedure and is the best way in selecting the optimum isotherm. To perform this, *xlstat* software is used which is an add-in software with Microsoft's excel spread sheet, Microsoft, and highly efficient than the solver add-in. The abilities of
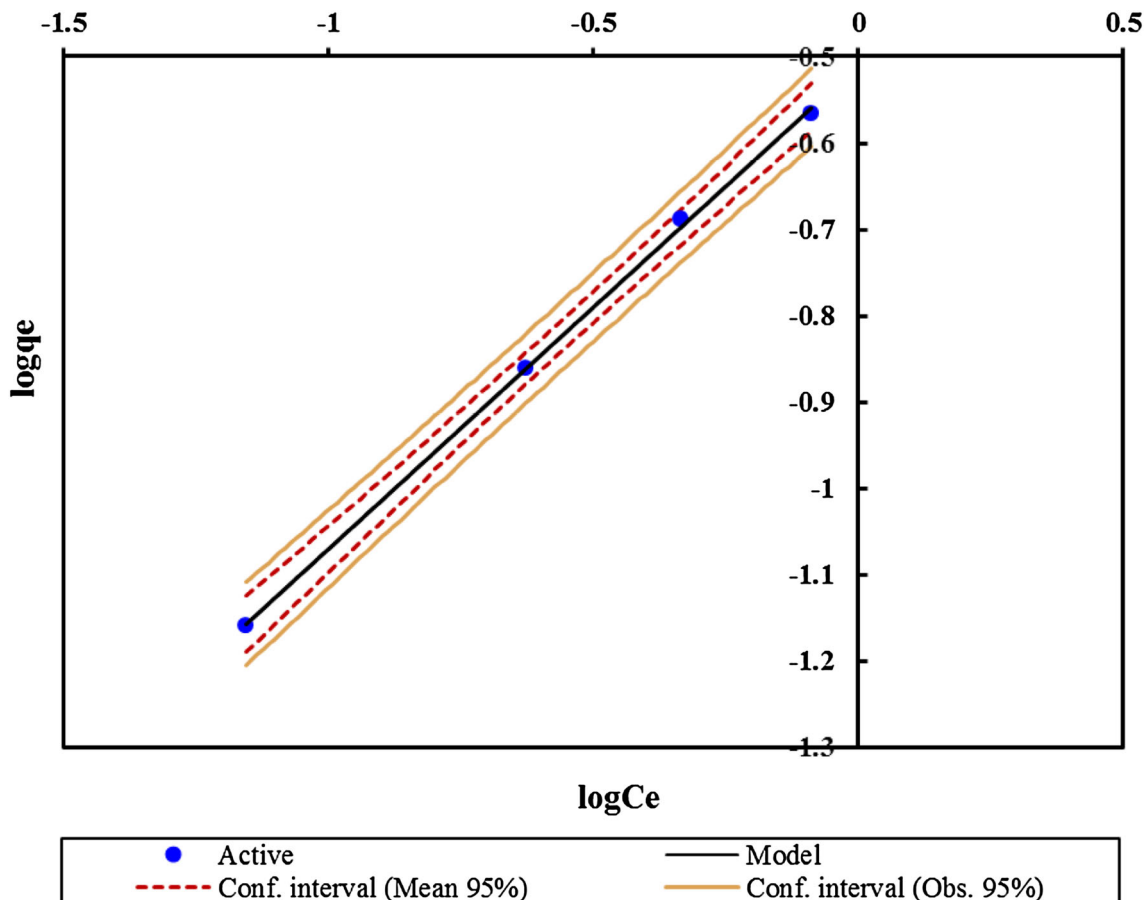

Fig. 2 Freundlich isotherm obtained using the linear method for the sorption of fluoride onto Bio-F
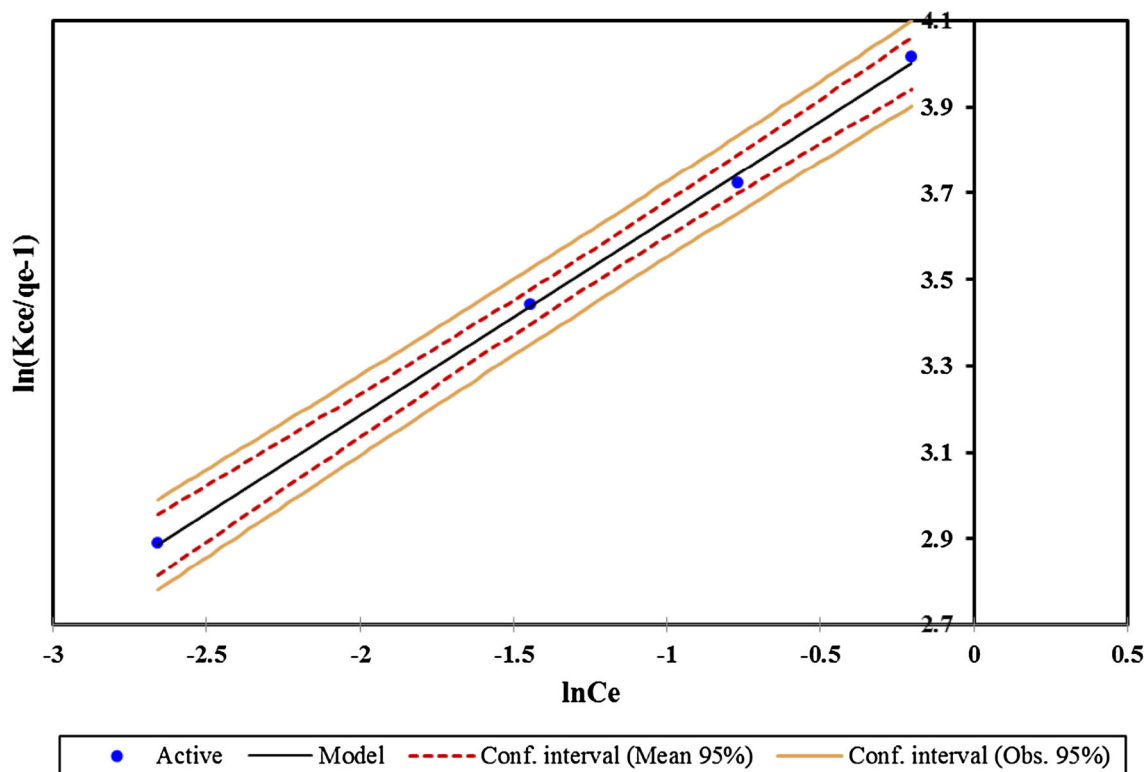
Fig. 3 Redlich–Peterson isotherm obtained using the linear method for the sorption of fluoride onto Bio-F

three used isotherms, i.e., Freundlich, Langmuir, and Redlich–Peterson isotherms were examined to model the equilibrium sorption data of fluoride onto Bio-F. The obtained results from the four linear Langmuir equations were observed to be quite similar with each other. When using the non-linear method, there were no problems with non-linear Langmuir isotherm equations as they were in the same error structures. The Langmuir constants obtained from non-linear and linear methods differed even when compared with the results of Langmuir-1 isotherm, which had the highest coefficient of determination for any Langmuir isotherm (Table 2). It seems that the isotherm obtained from Langmuir-1 provided the best fit to the experimental data as compared to other Langmuir linear equations because it had the highest coefficient of determination. The values of Langmuir constants, i.e., K_a and q_m were found to be close to those obtained by using the non-linear method. Figure 4 shows that the Redlich–Peterson isotherm, with almost similar coefficients of determination, seems to be the best-fit model for the experimental data. It has been reported that it is inappropriate to use the coefficient of determination of a linear regression analysis to compare the best-fitting models of different isotherms (Ho 2006a, b; Maliyekkal et al. 2006). Inversely, the linear regression has produced a vast amount of different outcomes. Consequently, the Redlich–Peterson isotherm was found to be the best-fit model for the present

sorption system. Unlike the linear analysis, a different isotherm would significantly affect the r^2 value and will have an impact on determination of other parameters, whereas the use of the non-linear method would avoid such errors.

Comparative account of linear and non-linear regression method

In this study, it is important to mention here that predicting the optimum isotherm by using only linear method is not appropriate (Yadav et al. 2014), as different forms of one single Langmuir equation may be applicable for a particular adsorption system. Subsequently, the results produced by these four equations may differ significantly as shown in Table 2. The probable reason behind unlike outcomes of different linearized forms of one equation may be the variation in derived error functions. Moreover, the error distribution may vary depending on the way of linearization. The same has been evidenced for the equilibrium sorption data of present adsorption system. However, another possible reason behind the variable results may be the different axial settings, which alter the result of linear regression and influence the determination process. Thus, it can be concluded that it is more appropriate to use non-linear method to estimate the parameters of an isotherm or a rate equation (Kumar and Sivanesan 2007). Also, non-
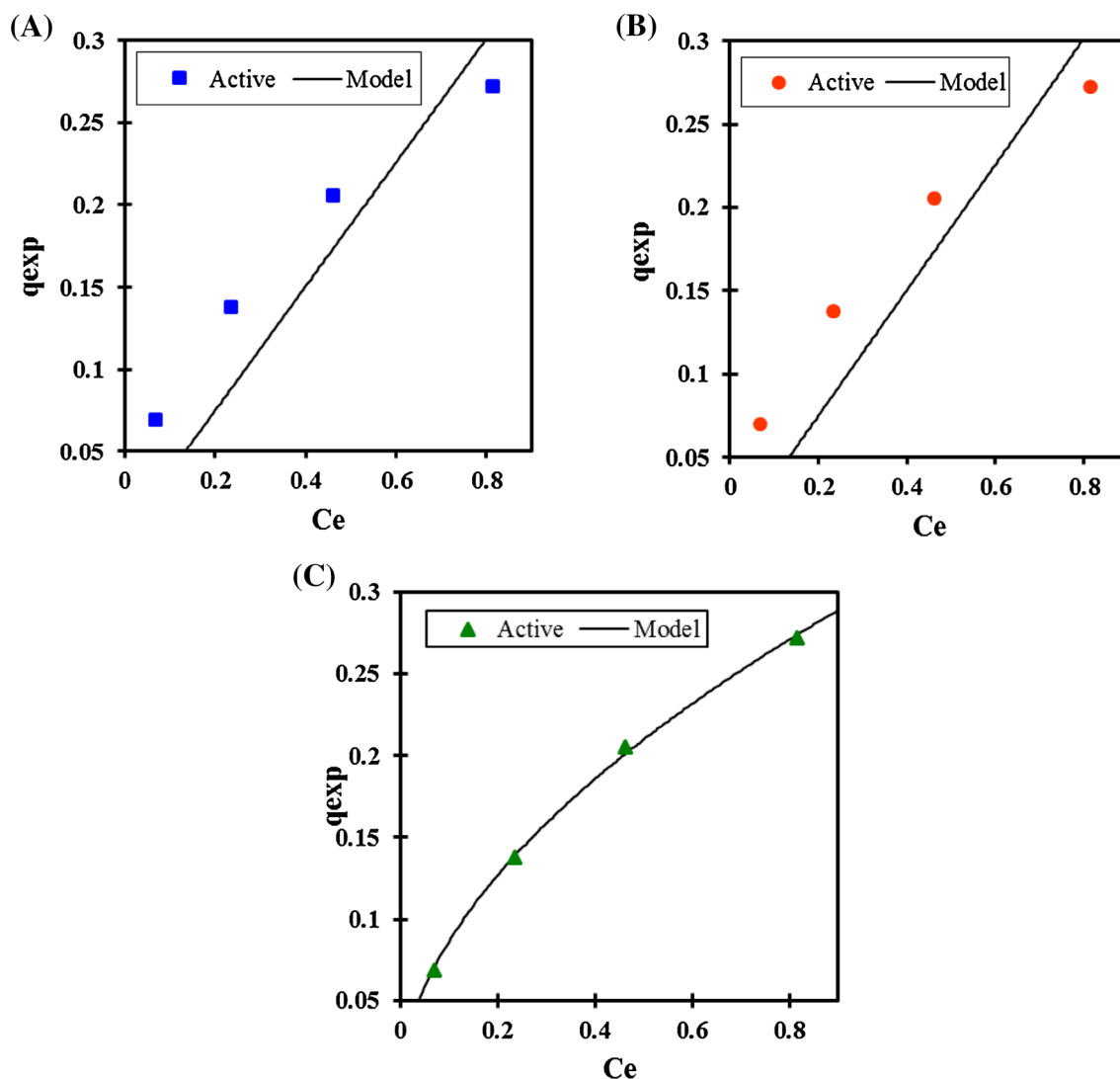
Fig. 4 Isotherms obtained using the non-linear method for the fluoride adsorption onto Bio-F: **a** Langmuir, **b** Freundlich, **c** Redlich–Peterson

linear method had an advantage that the error distribution does not get altered as in case of linear technique, because all the equilibrium parameters are fixed on the same axis.

Conclusions

Following conclusions can be drawn from this study:

- The equilibrium sorption data of F onto Bio-F sorbent is explained using the linear and non-linear forms of Langmuir, Freundlich and Redlich–Peterson isotherms.
- The comparison of linear and non-linear regression method shows that non-linear regression is more reliable as compared to linear regression method for the prediction of best-fit isotherm as well as parameter determination for the adsorption of F onto Bio-F.

- The values of r^2 of Langmuir-1 and Langmuir-2 presented in this study are close to those of the non-linear form of Langmuir isotherm, while Langmuir-3 and Langmuir-4 showed almost similar r^2 values. The values of r^2 of linear forms of Freundlich isotherm were observed to be different in comparison to the value of non-linear form of the Redlich–Peterson isotherm.
- Redlich–Peterson isotherm was found to be the best-fit among the investigated isotherms suggesting that the isotherms are approaching the Freundlich, but not the Langmuir isotherm on basis of β value which is not close to unity.

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