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Arsenic adsorption onto iron oxide-coated cement (IOCC): Regression analysis of equilibrium data with several isotherm models and their optimization

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Abstract

The present work examines the equilibrium sorption of arsenic (III and V) from aqueous environment onto iron oxide-coated cement (IOCC) at 288, 298 and 308 K, and determines the equilibrium sorption isotherms. The equilibrium for both As(III) and As(V) was achieved in 2 h. The experimental isotherm data were analysed using Langmuir, Freundlich, Dubinin–Radushkevich (D–R), Toth and Temkin isotherm equations. In order to determine the best-fit isotherm for each system, both linear and non-linear regressions were carried out. For this, six error analysis methods were used to evaluate the data: the linear coefficient of determination, the sum of the squares of errors, the sum of absolute errors, the average relative error, the hybrid fractional error function and the Marquardt's percent standard deviation. The error values indicated that the Freundlich isotherm was able to provide the best quality of fit for all the experimental data, over the concentration range studied, for both As(III) and As(V) at 288, 298 and 308 K. The values of the parameter sets of the isotherms also indicated that the adsorption of arsenic onto IOCC is a temperature dependent phenomena with As(III) and As(V) exhibiting exothermic and endothermic nature of adsorption, respectively.

Keywords: Adsorption; Arsenic; Error analysis; Isotherm; Equilibrium

1. Introduction

Arsenic is a toxic and carcinogenic metalloid that is introduced in the aqueous system through natural as well as anthropogenic sources. Contamination of potable ground water with arsenic and its removal in water treatment have become the focus of increasing attention worldwide. Elevated arsenic concentrations in excess of 10 $\mu g\, l^{-1}$ (the maximum level recommended for potable waters by the World Health Organization, 1993 [1]) have been found in different parts of the world [2]. In natural waters, usually inorganic arsenic in the form of As(III) and/or As(V) is found to be prevalent and is more toxic than organic arsenic. Long-term intake of arsenic contaminated water is highly detrimental to human beings resulting in severe and permanent impairment of human health [3,4]. This has promulgated the enforcement of stringent limits on the presence of arsenic in drinking water by various regulatory agencies and extensive research on arsenic treatment technologies with varying levels of success.

Among the numerous treatment technologies [5] developed for the removal of arsenic from the aqueous environment, adsorption is receiving increasing attention in becoming an attractive and promising technology because of its simplicity, cheaper pollution control method, ease of operation and handling, sludge free operation, and regeneration capacity. Detailed information on equilibrium properties is required for the design of adsorbers. The adsorption equilibrium provides fundamental physicochemical data for evaluating the applicability of sorption processes as a unit operation. An isotherm equation, whose parameters express the surface properties and affinity of the sorbent, at a fixed temperature and pH, usually describes the sorption equilibrium. Thus, an accurate mathematical description of the equilibrium isotherm is essential for effective design of adsorption contact processes.

This paper reports the equilibrium adsorption of arsenic (both +3 and +5 valence states) onto iron oxide-coated cement (IOCC), as adsorbent, at temperatures 288, 298 and 308 K. This adsorbent has been found to be very effective in the removal

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of arsenic from synthetic as well as from real life groundwater samples [6].

The present study investigates the effect of the isotherm type and the method used in deriving the isotherm parameters on the predictions by the parameters within the models. In order to develop IOCC as a suitable adsorbent for arsenic removal, it is very essential to understand its sorption capacity and equilibrium characteristics.

Throughout the years, until relatively recently, the quality of the isotherm fit to the experimental data was assessed based on the magnitude of the correlation coefficient for the linear regression and the isotherm giving an R^2 value closest to unity was deemed to provide the best-fit. However, the linearisation of adsorption isotherm equations using such data transformations would implicitly alter the error structure and could also violate the error variance and normality assumptions of standard least squares [7].

As an alternative to the linear transformation, non-linear optimization has also been applied by various researchers [7–14] to determine isotherm parameter values which require an error function assessment, in order to evaluate the fit of the isotherm to the experimental results for the removal of variety of components from the aqueous environment. However, there is very little detailed information in the literature in this regard on arsenic sorption by various adsorbent media.

For the present study, five widely used adsorption isotherms, four two-parameter equations – the Freundlich, Langmuir, Temkin and Dubinin–Radushkevich (D–R) isotherms – and one three-parameter equation – the Toth isotherm – were examined for arsenic sorption onto IOCC for their ability to model the equilibrium sorption data at temperatures 288, 298 and 308 K. The sets of isotherm parameters were determined using both linear regressions of transformed isotherms as well as non-linear regression. Five different error functions were examined and in each case the isotherm parameters were determined by minimizing the respective error function across the concentration range studied using the solver add-in with Microsoft's spreadsheet, Excel 2003 (Microsoft Corporation).

2. Materials and methods

2.1. Adsorbent

The principal adsorbent used in the study is iron oxide-coated cement (IOCC), a Ca–Al–Si–Fe–O containing complex substance. Cement is a commercially available material that served as a very good matrix over which the iron-oxide coating could be done effectively to optimize the sorptive capacity. The release of some amount of Ca^{2+} (one of the main constituents of the cement) in the form of $Ca(OH)_2$ from the adsorbent material helped in maintaining a near-surface pH in the alkaline range which was favourable for adsorption of both As(III) and As(V). The concentration of Ca^{2+} in the effluent, however, was found to be within the taste threshold (100–300 mg l^{-1}) set by WHO, 2004 [15].

IOCC was prepared by heating a mixture of 100 g white cement granules (geometric mean size = 212 μm) in a solution of $Fe(NO_3)_3{\cdot}9H_2O$, obtained by dissolving 50 g $Fe(NO_3)_3{\cdot}9H_2O$ in 150 ml water, at 100 °C for 16 h. The detailed procedure for the preparation and characterization of IOCC has been discussed elsewhere [5].

The composition of the adsorbent, as obtained from the chemical as well as the energy dispersive X-ray (EDX) analysis (Oxford ISIS-300 model), was MgO 0.58%, Al_2O_3 11.06%, quartz 9.72%, CaO 55.11%, Fe-oxide 23.53%. The bulk density, porosity and specific gravity were found to be 1.43 g cm^{-3}, 0.56 fraction and 2.54, respectively. The pH of the point of zero charge (pH_{ZPC}) was found to be 11.1. The presence of portlandite [$Ca(OH)_2$] (20–25%), amorphous calcium–silica–hydrate [C–S–H] (60–70%), iron oxides with predominant peaks of the Fe_3O_4 variety, iron silicate hydrate ($Ca_4Fe_{47}Si_{72}O_{180}(OH)_{36}{\cdot}xH_2O$), iron hydroxide:calcium ($Ca_3Fe_2(OH)_{12}$) and iron nitrate hydroxide ($Fe_4NO_3(OH)_{11}$) is indicated by the X-ray diffraction pattern of the IOCC *d*-spacing values, presented elsewhere [16].

Iron leaching from the iron coating of the adsorbent obtained from the leachability test was found to be very insignificant in the range of 0.018–0.02 mg l^{-1}.

One of the most important controls on adsorption of As(III) and As(V) is pH; pH has a major influence on aqueous arsenic speciation and on the composition of surface functional groups through protonation and deprotonation reactions [17]. At pH values less than the pH_{ZPC} of the adsorbent, the net charge is positive, facilitating the adsorption of anions. However, the effect of pH on arsenic adsorption differs between As(III) and As(V). The pH_{ZPC} of the adsorbent has been found to be 11.1 [16]. At pH range between 3 and 6, As(V) occurs mainly in the monovalent form of $H_2AsO_4^-$, while at higher pH values (>8) a divalent anion $HAsO_4^{2-}$ dominates; in the intermediate region of pH 6–8, both species co-exist [18]. So it is evident that in the pH range of natural waters, As(V) remains in the anionic state which is highly favourable for adsorption as the adsorbent surface remains positively charged at that pH range owing to its higher pH_{ZPC}. Compared to As(V), As(III) removal mechanism is somewhat more complicated. This is due to the fact that in the pH range of 6.5–7.5, which is generally the pH range of natural waters, As(III) predominantly exists as an uncharged ($H_3AsO_3^0$) species. However, at an alkaline pH range of 7.5–9.0, this uncharged specie dissociates as $H_3AsO_3^0 = H_2AsO_3^- + H^+$. As the adsorbent's pH in water is 8.5–9, it assists in the dissociation of the As(III) specie. After dissociation the negative arsenic specie is attracted to the positively charged adsorbent surface thus aiding in As(III) removal.

2.2. Adsorbates

The two inorganic forms of arsenic: As(III) and As(V) in single component aqueous solutions were used to assess experimental behaviour during the equilibrium adsorption studies. As(III) and As(V) stock solutions (1000 mg l^{-1}) were prepared by dissolving $NaAsO_2$ (LOBA Chemie) and $Na_2HAsO_4{\cdot}7H_2O$ (Nice Chemicals Pvt. Ltd.), respectively, in double distilled water. Experimental solutions of the desired concentration were obtained by successive dilutions with double distilled water.

2.3. Analysis

Concentrations of arsenic were determined by finding out the absorbance at the characteristic wavelength (535 nm) using a UV/vis spectrophotometer (Thermospectronic, Model no. UV-1, UK), by the silver dithiodiethylcarbamate method (minimum detectable quantity: 1 μg As), commonly known as the SDDC method [19].

2.4. Adsorption isotherms

Adsorption isotherms for this study were carried out at 288, 298, and 308 K using a completely mixed batch reactor (CMBR) method. Data for sorption isotherms were generated by contacting a fixed amount of IOCC with arsenic-containing aqueous solutions. A 50 ml of arsenic solutions at natural pH values with varying initial arsenic concentrations (0.7, 1.4, 2.7, 5.4, 13.5 $\mathrm{mg\,l^{-1}}$ for As(III), and 0.5, 1, 2, 4, 10 $\mathrm{mg\,l^{-1}}$ for As(V)) and a constant mass of accurately weighed IOCC (1.5 g for As(III) and 0.15 g for As(V)) were placed in 150 ml capacity polyethylene bottles (Tarson Co. Ltd., India). The optimum dose of 1.5 g for As(III) and 0.15 g for As(V) in 50 ml solution was previously determined from preliminary experiments. The test bottles were then shaken in the BOD incubator shaker at a speed of 180 ± 10 rpm at the desired temperatures for 2 h. Preliminary experiments on both As(III) and As(V) at various concentration ranges indicated that the adsorption equilibrium was reached in 2 h. Based on these results, the equilibrium time for the isotherm studies were chosen as 2 h [16,20]. At the end of the experiment, the samples were filtered out using Whatman 42 filter paper and the filtrate analysed for residual arsenic after adsorption. The equilibrium sorption capacity was determined from $q_e = (C_i - C_e)/m$ where C_i ($\mathrm{mg\,l^{-1}}$) is the initial concentration, C_e the equilibrium concentration ($\mathrm{mg\,l^{-1}}$) and m is the adsorbent dose ($\mathrm{g\,l^{-1}}$).

3. Theory

3.1. Adsorption isotherms

The successful representation of the dynamic adsorptive separation of solute from solution onto an adsorbent depends upon an appropriate description of the equilibrium separation between the two phases. Adsorption equilibrium is established when the amount of solute being adsorbed onto the adsorbent is equal to the amount being desorbed and the equilibrium solution concentration remains constant at this point. By plotting solid phase concentration against liquid phase concentration it is possible to depict the equilibrium adsorption isotherm.

Various isotherm equations have been used to describe the equilibrium characteristics of adsorption. Both the sorption mechanism and the surface properties and affinity of the sorbent can be understood from the equation parameters and the underlying thermodynamic assumptions of these isotherm models.

3.1.1. Langmuir isotherm

The Langmuir isotherm [21] theory assumes that the sorption takes place at specific homogeneous sites within the adsorbent, i.e. once a sorbate molecule occupies a site, no further adsorption can take place at that site:

$$q_e = \frac{bQ_0C_e}{1+bC_e} \tag{1}$$

where C_e is the equilibrium concentration ($\mathrm{mg\,l^{-1}}$), q_e the amount of arsenic sorbed ($\mathrm{mg\,g^{-1}}$), Q_0 the theoretical monolayer capacity ($\mathrm{mg\,g^{-1}}$), and b is the sorption equilibrium constant ($\mathrm{l\,mg^{-1}}$) related to the energy of adsorption. At low sorbate concentrations, the Langmuir isotherm effectively reduces to a linear isotherm and thus follows Henry's law [11].

3.1.2. Freundlich isotherm

The Freundlich isotherm [22] is the earliest known relationship describing the sorption equation. It assumes that as the adsorbate concentration in solution increases so too does the concentration of adsorbate on the adsorbent surface and therefore, has an exponential expression [23]:

$$q_e = K_F C_e^{1/n} \tag{2}$$

In this equation K_F and n are the Freundlich constants representing the adsorption capacity and the adsorption intensity, respectively. The Freundlich isotherm is often criticized for lacking a fundamental thermodynamic basis since it does not reduce to Henry's law at low concentrations [11].

3.1.3. Dubinin–Radushkevich (D–R) isotherm

The D–R approach assumes that there is a surface area where the adsorption energy is homogeneous. The D–R isotherm [24] has the form:

$$\begin{aligned} q_e &= Q_m \exp\left(-K\left[RT\ln\left(1+\frac{1}{C_e}\right)\right]^2\right) \\ &= Q_m \exp(-K\varepsilon^2) \end{aligned} \tag{3}$$

where ε (Polanyi potential) = $RT\ln(1+1/C_e)$, Q_m is the D–R constant, K is related to the mean free energy of sorption per mole of the sorbate when it is transferred to the surface of the solid from infinity in the solution and this energy can be computed using the following relationship [25]:

$$E = \frac{1}{\sqrt{2K}}. \tag{4}$$

3.1.4. Toth isotherm

Tóth isotherm [26] was developed to improve the fitting of the Langmuir isotherm to experimental data based on the premise that there exists site heterogeneity on the sorbent and that most sites have sorption energy lower than the maximum adsorption energy. The Tóth correlation in a form applicable to liquid-phase adsorption is given in Eq. (10):

$$q_e = \frac{q_m C_e}{[a_t + C_e^t]^{1/t}}, \quad 0 < t \le 1 \tag{5}$$

where q_m is the adsorbed amount ($\mathrm{mg\,g^{-1}}$), a_t the adsorptive potential constant $(\mathrm{mg\,l^{-1}})^t$ and t characterizes the heterogeneity coefficient of the adsorbent. If surface is homogeneous, then $t = 1$, so the Toth equation reduces to the Langmuir equation.

3.1.5. Temkin isotherm

The Temkin isotherm was derived assuming that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation [27]. It is expressed as [28]

$$q_e = \frac{RT}{b}\ln(K_T C_e) = B_1 \ln(K_T C_e) \tag{6}$$

where constant $B_1 = RT/b$ is related to the heat of adsorption, R the universal gas constant ($\mathrm{J\,mol^{-1}\,K^{-1}}$), T the temperature (K), b the variation of adsorption energy ($\mathrm{J\,mol^{-1}}$) and K_T is the equilibrium binding constant ($\mathrm{l\,mg^{-1}}$) corresponding to the maximum binding energy.

The Temkin isotherm equation assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent–adsorbate interactions, and that the adsorption is characterized by a uniform distribution of the binding energies, up to some maximum binding energy.

3.2. Determination of isotherm parameters

The isotherm parameters were determined by both linear regression as well as non-linear regression.

3.2.1. Linear regression

For the determination of parameters by linear regression, the isotherm parameters were so transformed that the equations were first converted to their linearised forms and then linear regression was applied. This method is very simple for a two-parameter isotherm equation but a linear analysis is not always possible for a three-parameter isotherm.

3.2.2. Non-linear regression

The quality of the isotherm fit to the experimental data and hence the isotherm parameters obtained using linear regression are typically assessed based on the magnitude of the correlation coefficient for the regression, i.e. the isotherm with R^2 value nearer to unity is deemed to provide the best-fit. However, due to the inherent bias resulting from linearisation, non-linear regression was applied to determine alternative isotherm parameter sets.

In order to evaluate the fit of the isotherm equation to the experimental equilibrium data, an error function is required to enable the optimization procedure. The isotherm parameters derived can be affected by the choice of error function viz., error functions based primarily on absolute deviation bias the fit towards high concentration data and this weighting increases when the square of the deviation is used to penalize extreme errors. By dividing the deviation by the measured value this bias can be reduced partly in order to emphasize the significance of fractional deviations.

The five non-linear error functions employed in this study are as follows:

1. The sum of the squares of the errors (SSE):

$$\mathrm{SSE} = \sum_{i=1}^{n} (q_{e,\mathrm{calc}} - q_{e,\mathrm{exp}})_i^2 \tag{7}$$

2. The sum of the absolute errors (SAE):

$$\mathrm{SAE} = \sum_{i=1}^{n} |q_{e,\mathrm{calc}} - q_{e,\mathrm{exp}}|_i \tag{8}$$

3. The average relative error (ARE):

$$\mathrm{ARE} = \frac{100}{n}\sum_{i=1}^{n} \left|\frac{q_{e,\mathrm{exp}} - q_{e,\mathrm{calc}}}{q_{e,\mathrm{exp}}}\right|_i \tag{9}$$

4. The hybrid fractional error function (HYBRID) [7]:

$$\mathrm{HYBRID} = \frac{100}{n-p}\sum_{i=1}^{n} \left[\frac{(q_{e,\mathrm{exp}} - q_{e,\mathrm{exp}})^2}{q_{e,\mathrm{exp}}}\right]_i \tag{10}$$

5. Marquardt's percent standard deviation (MPSD) [29]:

$$\mathrm{MPSD} = 100\sqrt{\frac{1}{n-p}\sum_{i=1}^{n} \left(\frac{q_{e,\mathrm{exp}} - q_{e,\mathrm{calc}}}{q_{e,\mathrm{exp}}}\right)_i^2} \tag{11}$$

Since the application of these five different error methods will produce different isotherm parameter sets, it is difficult to directly identify an overall optimum parameter set. Hence, in order to be able to perform a meaningful comparison between the parameter sets, for each parameter set for each isotherm a procedure of normalising and combining the error results was adopted resulting in a so-called 'sum of the normalised errors (SNE)'.

The 'sum of the normalised errors' for each isotherm was calculated by:

(a) selecting one error function at a time and determining the isotherm parameters that minimise that error function to produce the isotherm parameter set for that error function;
(b) determining the error values for all the other error functions for that isotherm parameter set;
(c) calculating all other parameter sets for each error function and all their associated error function values;
(d) selecting each error measure in turn and dividing the errors determined for a given parameter set by the maximum for that error function to get the normalized errors; and
(e) summing all these normalised errors for each parameter set.

This method allows a direct comparison of the scaled errors and hence identifies the isotherm parameter that would provide the closest fit to the measured data.

4. Results and discussion

4.1. Langmuir isotherm

The sorption data were analysed according to the linear as well as non-linear form of the isotherm. The linear plots of $1/q_e$

Table 1
Linear and non-linear Langmuir isotherm parameters for As(III) at temperatures 288, 298 and 308 K

	LTFM	SSE	SAE	ARE	HYBRID	MPSD
288 K						
b	0.435	0.002625	0.144128	0.443295	0.024038	0.244286
Q_0	0.727	89.79098	2.05893	0.706252	10.063	1.187123
SSE	0.00903	**0.000787**	0.002276	0.009919	0.000898	0.003882
SAE	0.121942	0.055632	**0.054404**	0.123931	0.056976	0.09054
ARE	9.573652	14.6774	9.25385	**9.124632**	13.98529	9.826834
HYBRID	0.850197	0.2591	0.499379	0.906987	**0.256559**	0.457305
MPSD	16.65093	21.38642	18.41434	16.7111	20.1208	**14.97536**
SNE	4.262557	2.813909	**2.710548**	4.403067	2.726809	2.995889
298 K						
b	0.409	0.002241	0.093555	0.456348	0.002478	0.15073
Q_0	0.689	100.6879	2.873624	0.617083	89.71549	1.68194
SSE	0.012702	**0.000926**	0.002293	0.015606	0.000977	0.003401
SAE	0.135746	0.059611	**0.05047**	0.142842	0.055392	0.088716
ARE	10.21595	11.26981	10.0133	**9.98684**	11.98446	10.86367
HYBRID	1.127933	0.230195	0.526319	1.35161	**0.225925**	0.410622
MPSD	18.22647	17.52871	19.51578	19.29552	17.96021	**15.04087**
SNE	4.385119	**2.485519**	2.725183	4.822029	2.537833	2.819992
308 K						
b	0.383	0.001638	0.060255	0.484653	0.00151	0.080109
Q_0	0.671	134.4350	4.175776	0.536302	142.07122	2.87161
SSE	0.015954	**0.001035**	0.002149	0.022105	0.001167	0.002627
SAE	0.141467	0.058489	**0.054052**	0.154641	0.058352	0.080191
ARE	9.809719	10.35047	9.537305	**9.493222**	10.59759	10.53804
HYBRID	1.377545	0.225589	0.511324	1.885487	**0.211438**	0.329879
MPSD	19.41689	14.95621	19.72512	22.21565	15.15964	**14.16893**
SNE	4.166825	**2.194601**	2.505783	4.895791	2.224657	2.444532

Table 2
Linear and non-linear Langmuir isotherm parameters for As(V) at temperatures 288, 298 and 308 K

	LTFM	SSE	SAE	ARE	HYBRID	MPSD
288 K						
b	1.198	0.588576	0.870021	1.06681	0.772638	1.01991
Q_0	3.39	5.38999	4.55937	3.74659	4.64435	3.89940
SSE	0.230844	**0.033535**	0.069229	0.131121	0.044731	0.102891
SAE	0.658256	0.345715	**0.306076**	0.54831	0.387071	0.503513
ARE	8.15724	14.16462	7.58020	**6.231645**	10.40904	7.462063
HYBRID	3.24666	1.89156	2.031793	2.223272	**1.492385**	1.96726
MPSD	12.92695	21.10184	13.52154	12.07694	14.49796	**11.99585**
SNE	4.188487	3.253087	**2.566611**	3.098029	2.663374	2.911854
298 K						
b	1.147	0.753570	0.748281	0.774762	0.772673	0.812432
Q_0	3.86	5.45340	5.47426	5.38455	5.37998	5.21039
SSE	0.193537	**0.000364**	0.000372	0.000553	0.000476	0.00169
SAE	0.488683	0.034953	**0.032703**	0.03929	0.043148	0.071708
ARE	4.84220	2.00397	2.009598	**1.940782**	1.984516	2.074678
HYBRID	2.30368	0.035295	0.038302	0.03176	**0.030589**	0.046135
MPSD	9.47993	4.16223	4.344374	3.508335	3.623228	**3.257939**
SNE	5	0.941639	0.958758	**0.867929**	0.896069	0.947621
308 K						
b	1.023	1.21996	1.18942	1.02117	1.17115	1.12521
Q_0	4.63	4.11259	4.14147	4.62924	4.18175	4.27125
SSE	0.030365	**0.002384**	0.002694	0.029692	0.002877	0.004443
SAE	0.231229	0.087644	**0.079749**	0.229779	0.089492	0.109142
ARE	2.76259	3.349283	2.537228	**2.083713**	2.383099	2.737292
HYBRID	0.405365	0.117839	0.098518	0.398871	**0.095869**	0.111638
MPSD	4.38614	5.072622	3.895983	4.377029	3.622495	**3.20008**
SNE	4.689499	2.748246	2.202233	4.440556	**2.143927**	2.341859

Table 3
Comparison of regression coefficients of linear isotherms for As(III) and As(V) adsorption onto IOCC at temperatures 288, 298 and 308 K

Linear isotherm	As(III)			As(V)		
	288 K	298 K	308 K	288 K	298 K	308 K
Langmuir	0.997	0.998	0.998	0.998	0.999	0.999
Freundlich	0.993	0.993	0.992	0.988	0.993	0.978
Dubinin–Radushkevich	0.892	0.879	0.873	0.943	0.937	0.955
Temkin	0.811	0.798	0.793	0.903	0.908	0.942

against $1/C_e$ for As(III) and As(V) are shown in Fig. 1(a) and (b) and the linear isotherm constants b, Q_0, for the adsorption of As(III) and As(V) onto IOCC at temperatures 288, 298 and 308 K, are presented in the linear transform (LTFM) columns of Tables 1 and 2, respectively. This isotherm was found to be linear over the whole concentration range studied with very high correlation coefficients (Table 3) for both As(III) and As(V). The R^2 values suggest that the Langmuir isotherm provides a good model of the sorption system. The sorption capacity, Q_0, decreases with the increase in temperature from 288 to 308 K indicating exothermic nature of sorption for As(III) and increases with the increase in temperature indicating endothermic nature of sorption for As(V).

The Langmuir isotherm constants for As(III) and As(V) determined by non-linear regression using five different error functions are presented in Tables 1 and 2, respectively. The results demonstrate that the values of the constants b and Q_0 obtained by non-linear regression are not all consistent and have no similarity with the linear transform values. The only parameter values that are somewhat close to those obtained by linearisation are the ARE set for As(III) at all temperatures studied and for As(V) at 288 and 308 K. Considering the wide range of variation in the isotherm parameters together with the comparative magnitude of the error values suggests that the Langmuir isotherm does not provide a particularly good model for sorption of arsenic onto IOCC. Finally, as indicated by the sum of normalised errors, the parameter set that produces the best overall fit for As(III) are SAE at 288 K, SSE at both 298 and 308 K and for As(V), SAE at 288 K, ARE at 298 K and HYBRID at 308 K.

4.2. Freundlich isotherm

The linear Freundlich isotherm plots for the sorption of arsenic on IOCC are presented in Fig. 2(a) and (b). A careful examination of the plots suggests that the linear Freundlich isotherm is also a good model for the sorption of arsenic, at all the temperatures studied, next to Langmuir. The coefficients of determination (R^2) values presented in Table 3 support this fact, with As(III) isotherms giving seemingly better fits of the experimental data than As(V). The LTFM columns of Tables 4 and 5 give the isotherm constants, K_F and $1/n$. As is evident from Table 4, the K_F value gradually decreases with the increase of

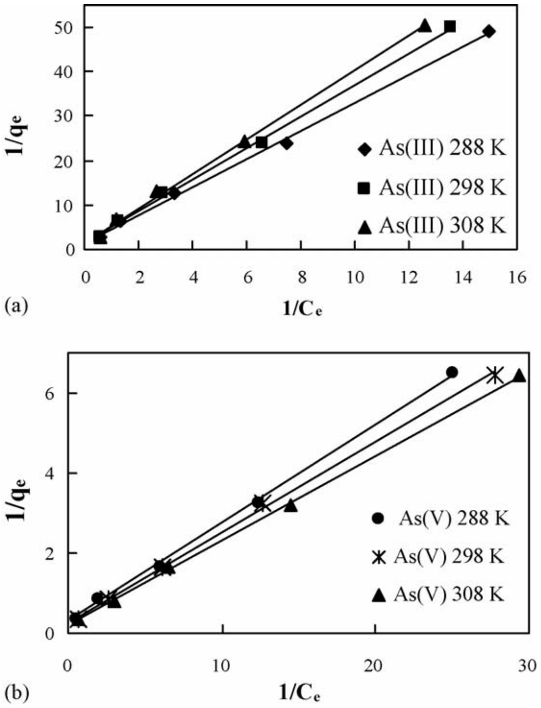

Fig. 1. (a) Langmuir isotherms (Eq. (1)) of As(III) sorbed on IOCC; (b) Langmuir isotherms (Eq. (1)) of As(V) sorbed on IOCC.

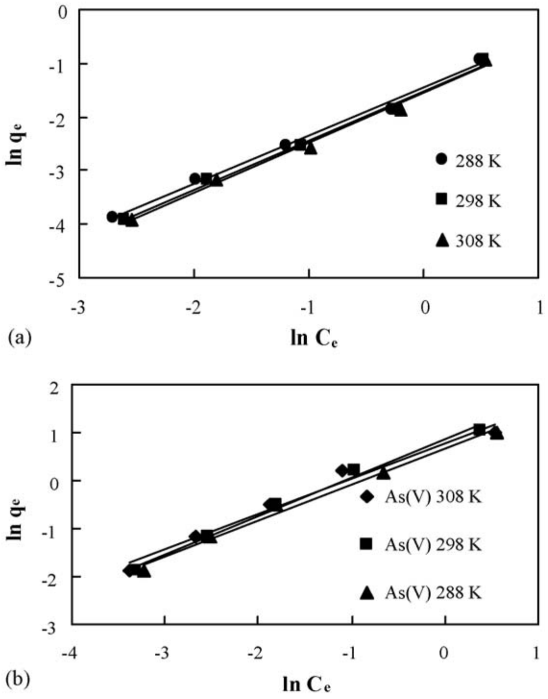

Fig. 2. (a) Freundlich isotherms (Eq. (2)) of As(III) sorbed on IOCC; (b) Freundlich isotherms (Eq. (2)) of As(V) sorbed on IOCC.

Table 4
Linear and non-linear Freundlich isotherm parameters for As(III) at temperatures 288, 298 and 308 K

	LTFM	SSE	SAE	ARE	HYBRID	MPSD
288 K						
K_F	0.231	0.232678	0.247058	0.238246	0.234464	0.226227
1/*n*	0.8911	1.03348	0.940152	0.909881	0.937359	0.883816
SSE	0.001836	**0.000741**	0.001236	0.001286	0.001122	0.002364
SAE	0.063326	0.055337	**0.039586**	0.052361	0.057137	0.069885
ARE	6.764391	17.65973	7.165109	**6.166415**	9.605775	7.109278
HYBRID	0.242198	0.324886	0.275189	0.229801	**0.20991**	0.267791
MPSD	11.255972	26.65135	14.22044	12.08093	13.68997	**11.08715**
SNE	3.233664	4.105281	2.875625	**2.803041**	2.995915	3.642839
298 K						
K_F	0.217	0.219	0.231	0.201	0.222	0.212
1/*n*	0.9133	1.08934	1.01209	0.88526	0.979314	0.904642
SSE	0.00233	**0.000678**	0.000989	0.005331	0.001122	0.003022
SAE	0.071821	0.053545	**0.041375**	0.087457	0.055901	0.076643
ARE	7.485957	18.92481	11.12186	**7.003567**	10.3851	7.320427
HYBRID	0.280298	0.349623	0.2659	0.479615	**0.219629**	0.317771
MPSD	11.748716	29.94964	18.5572	12.52708	15.70299	**11.57481**
SNE	2.6305496	3.468390	2.420312	3.788345	**2.380646**	2.879070
308 K						
K_F	0.209	0.210753	0.220765	0.211772	0.214546	0.205075
1/*n*	0.9364	1.12364	1.05896	0.934047	1.012438	0.927384
SSE	0.002494	**0.000587**	0.000798	0.002257	0.001013	0.003174
SAE	0.074308	0.04979	**0.039817**	0.072773	0.055054	0.078745
ARE	8.083835	18.66432	12.43356	**7.810142**	11.05975	7.873579
HYBRID	0.286202	0.331779	0.25071	0.283053	**0.208074**	0.325908
MPSD	11.739015	30.38978	20.90166	12.10501	16.432	**11.60696**
SNE	3.41144	3.817234	2.866669	3.305166	**2.778714**	3.786093

Table 5
Linear and non-linear Freundlich isotherm parameters for As(V) at temperatures 288, 298 and 308 K

	LTFM	SSE	SAE	ARE	HYBRID	MPSD
288 K						
K_F	1.930927	1.866558	1.848022	1.846629	1.863344	1.912581
1/*n*	0.7441	0.692469	0.712170	0.713373	0.711775	0.749081
SSE	0.042702	**0.009005**	0.010868	0.011111	0.010705	0.038101
SAE	0.338649	0.17217	**0.133296**	0.134779	0.165412	0.316809
ARE	8.783485	10.44728	7.657433	**7.550525**	8.258035	8.53998
HYBRID	1.119174	0.862548	0.773727	0.777551	**0.762182**	1.118359
MPSD	13.81996	19.67352	15.64558	15.47088	15.97466	**13.61696**
SNE	4.543209	3.489983	2.867677	**2.862051**	3.022596	4.336616
298 K						
K_F	2.342925	2.208	2.191	2.142	2.218	2.309
1/*n*	0.7944	0.702640	0.705575	0.766812	0.746073	0.791996
SSE	0.104807	**0.015477**	0.016077	0.040012	0.025249	0.084041
SAE	0.488218	0.236605	**0.212296**	0.273686	0.300278	0.457531
ARE	7.817509	13.69685	12.65846	**7.208585**	9.679562	7.603845
HYBRID	1.617731	1.423455	1.308206	1.293149	**0.881130**	1.440715
MPSD	10.84894	25.55981	23.95912	12.35249	14.59817	**10.77239**
SNE	3.995205	3.512209	3.258464	2.751283	**2.678466**	3.606196
308 K						
K_F	2.214884	2.034951	1.988522	2.220227	2.027853	2.127149
1/*n*	0.7387	0.604959	0.626994	0.735967	0.668643	0.733730
SSE	0.319092	**0.053241**	0.060104	0.312969	0.080471	0.212593
SAE	0.831893	0.447764	**0.367130**	0.820949	0.485361	0.745275
ARE	13.06559	24.30175	18.33642	**12.96208**	15.12924	13.17678
HYBRID	4.972617	4.357222	3.244364	4.882317	**2.673857**	4.03622
MPSD	19.19446	44.60574	34.6527	19.32754	24.84811	**18.64119**
SNE	3.967954	3.581342	2.813522	3.9161739	**2.552964**	3.333937

temperature indicating exothermic nature of As(III) adsorption on IOCC. The K_F value in Table 5 shows an irregular increase from 288 to 308 K.

Tables 4 and 5 present the Freundlich isotherm constants determined by non-linear regression. From the results it is evident that the isotherm constants obtained by non-linear regression are more or less consistent and quite similar to the linear transform values of the isotherm. In each case, for both As(III) and As(V), the MPSD parameters are the closest to those obtained by linearization from which it can be inferred that the Freundlich model gives a reasonable approximation to the optimum parameter set obtained by non-linear regression. Comparing the values of the error measures of As(III) and As(V), it is evident from most of the error measures that the Freundlich isotherm produces a better fit to the As(III) data than it does for As(V). The sum of normalized errors indicate that the ARE parameter set produces the best overall fit for both As(III) and As(V) at 288 K and that the HYBRID parameter set produces the optimum fit for both As(III) and As(V) at 298 and 308 K.

4.3. Dubinin–Radushkevich (D–R) isotherm

Fig. 3(a) and (b) shows the sorption data analysed according to the linear form of the D–R isotherm. The examination of the

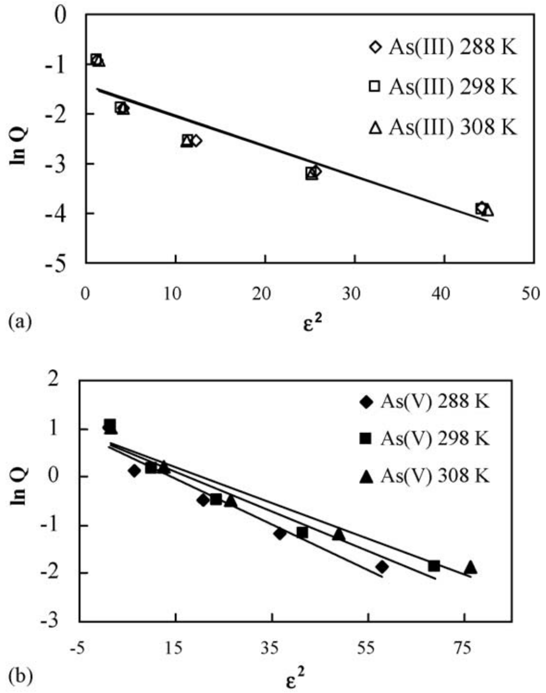

Fig. 3. (a) D–R isotherms (Eq. (3)) of As(III) sorbed on IOCC; (b) D–R isotherms (Eq. (3)) of As(V) sorbed on IOCC.

Table 6
Linear and non-linear D–R isotherm parameters for As(III) at temperatures 288, 298 and 308 K

	LTFM	SSE	SAE	ARE	HYBRID	MPSD
288 K						
Q_m	0.246	0.545742	0.474839	0.198298	0.322401	0.192361
K	0.0616	0.269469	0.145112	0.060736	0.101959	0.055282
E (kJ mol^{-1})	2.849					
SSE	0.030877	**0.006559**	0.01296	0.045073	0.016753	0.046988
SAE	0.252909	0.159145	**0.158463**	0.232509	0.21746	0.243155
ARE	30.30646	58.71995	47.67498	**20.7989**	41.3308	21.20808
HYBRID	3.281347	3.706855	3.865049	3.937852	**2.570387**	4.10304
MPSD	41.54759	92.50667	80.23211	37.66128	60.75749	**36.03777**
SNE	3.422110	3.672288	3.523589	3.599648	**3.203485**	3.712176
298 K						
Q_m	0.238	0.552	0.493	0.197	0.343	0.181
K	0.0611	0.275763	0.171232	0.061593	0.121103	0.054032
E (kJ mol^{-1})	2.861					
SSE	0.03303	**0.005918**	0.010409	0.045424	0.014518	0.051105
SAE	0.260103	0.156328	**0.152923**	0.238394	0.209848	0.260421
ARE	31.82158	57.72511	50.82637	**22.69821**	45.17916	23.02237
HYBRID	3.579055	3.454974	3.558608	4.051004	**2.676826**	4.499008
MPSD	44.50301	91.09247	82.96492	39.73859	69.04329	**37.92357**
SNE	3.480425	3.484032	3.373136	3.534133	**3.225474**	3.815147
308 K						
Q_m	0.234	0.555116	0.492859	0.197899	0.366617	0.175805
K	0.0604	0.269826	0.165759	0.062388	0.136308	0.053082
E (kJ mol^{-1})	2.877					
SSE	0.034133	**0.005429**	0.010451	0.045007	0.012129	0.053075
SAE	0.262508	0.148034	**0.147828**	0.239803	0.194712	0.269092
ARE	32.67833	56.77601	48.38554	**23.95338**	45.78898	24.24597
HYBRID	3.71373	3.253847	3.505723	4.06877	**2.636618**	4.696038
MPSD	45.93356	89.85532	81.99907	41.32047	73.1667	**39.01464**
SNE	3.496224	3.345305	3.257582	3.487319	**3.134327**	3.86124

Table 7
Linear and non-linear D–R isotherm parameters for As(V) at temperatures 288, 298 and 308 K

	LTFM	SSE	SAE	ARE	HYBRID	MPSD
288 K						
Q_m	1.97	2.971918	2.995301	1.687985	2.250003	1.712353
K	0.047	0.107214	0.072641	0.046419	0.056273	0.042166
E (kJ mol^{-1})	3.269					
SSE	0.877315	**0.306082**	0.512317	1.337831	0.580192	1.281402
SAE	1.319234	1.17001	**0.937632**	1.313543	1.212755	1.37821
ARE	20.63008	53.23531	35.46346	**18.40782**	26.67643	17.54698
HYBRID	12.70532	20.82727	18.57564	16.97053	**11.23813**	16.22397
MPSD	29.41674	81.97463	60.87157	32.04479	39.78121	**27.22374**
SNE	2.969393	4.077724	3.363892	3.504595	**2.839609**	3.398509
298 K						
Q_m	2.090	3.183	3.215	1.873	2.727	1.843
K	0.041	0.080283	0.070362	0.043252	0.059274	0.039525
E (kJ mol^{-1})	3.496					
SSE	0.877202	**0.120836**	0.168611	1.236269	0.24927	1.283116
SAE	1.354668	0.739791	**0.637715**	1.233543	0.917343	1.34698
ARE	23.85898	39.31806	31.86057	**17.76907**	28.73682	19.64792
HYBRID	12.83808	10.65784	9.367833	15.39551	**7.426708**	16.03751
MPSD	31.86301	66.61068	57.71851	32.57231	46.65739	**29.78963**
SNE	3.569319	3.304836	2.863116	3.774972	**2.765855**	3.941262
308 K						
Q_m	2.14	2.96948	3.006612	1.954118	2.658008	1.937829
K	0.037	0.062192	0.059636	0.037363	0.049431	0.035614
E (kJ mol^{-1})	3.686					
SSE	0.594313	**0.069428**	0.077442	0.849837	0.150542	0.876604
SAE	1.107971	0.533361	**0.477276**	1.066084	0.765162	1.130932
ARE	19.34202	31.889	28.95262	**15.67509**	25.82482	16.61247
HYBRID	9.106358	7.431681	6.81224	11.10024	**5.249805**	11.5594
MPSD	26.99814	58.3758	54.74037	26.89132	40.75854	**25.8295**
SNE	3.514488	3.193725	2.945330	3.824613	**2.810513**	3.963416

plots show that though the D–R isotherm shows good correlation with the sorption behaviour of As(V), it do not correlate as well with the sorption of As(III) and this is confirmed by the R^2 values presented in Table 3. Nevertheless its various parameters give certain information on the nature of the ongoing adsorption process. The linear transform (LTFM) columns of Tables 6 and 7 show the linear D–R isotherm constants for As(III) and As(V) sorption on IOCC, respectively. The values of E ($E < 8$ kJ mol^{-1}) calculated from Eq. (4) indicate that physisorption due to weak Van der Waals forces plays a significant role in the adsorption process. As is evident from the results in the LTFM column of Table 6, the values of the sorption capacity, Q_m decreases with increase in temperature which indicates the exothermic nature of the As(III) adsorption on IOCC. The values of Q_m in the LTFM column of Table 7, however denote an endothermic nature of As(V) sorption on IOCC as Q_m increases with increase in temperature.

The D–R isotherm constants obtained from the other five-error analysis methods are also presented in Tables 6 and 7. The parameter sets of all the error functions are significantly different from each other as well as from those obtained by linearization. The only parameter values that are slightly close to those obtained by linearization are the ARE set for both As(III) and As(V) at all temperatures studied. Based on the sum of normalized errors, the HYBRID parameter set produces the best fit for both the states of arsenic at all the three temperatures studied.

4.4. Toth isotherm

The five error methods mentioned in this study have been used to analyse this three parameter isotherm and the values of the isotherm parameters for As(III) and As(V) are presented in Tables 8 and 9, respectively.

As is evident from Table 8, the values of the parameter q_m does not vary significantly across the range of error methods but the values of a_t shows deviation over a wide range. However, in case of As(V), all the three isotherm parameter values do not show significant variation across the range of error methods used. The values of q_m in Table 8 shows a decrease with the increase in temperature indicating exothermic nature of adsorption for As(III) while in Table 9 it shows an increase with the increase in temperature indicating endothermic adsorption for As(V). The sums of the normalised errors indicate that the closest fits to As(III) adsorption onto IOCC experimental data at temperatures 288, 298 and 308 K are produced by HYBRID, SSE and SSE parameter sets, respectively. For As(V), HYBRID parameter sets produce the closest fit to the experimental data at all the three temperatures studied.

Table 8
Non-linear Toth isotherm parameters for As(III) at temperatures 288, 298 and 308 K

	SSE	SAE	ARE	HYBRID	MPSD
288 K					
q_m	1073.8475	1073.8817	1073.8804	1073.8712	1073.8817
t	0.832514	0.232982	0.236544	0.326949	0.228928
a_t	1112.2099	5.966560	6.379063	14.71084	5.945055
SSE	**0.000779**	0.002466	0.002448	0.001152	0.002991
SAE	0.065059	**0.053903**	0.07032	0.059446	0.075659
ARE	14.69136	13.28993	**6.638736**	11.07505	6.911519
HYBRID	0.389101	0.858389	0.44283	**0.349188**	0.48816
MPSD	26.26883	26.64142	14.49061	19.18616	**14.38109**
SNE	3.559653	4.441529	3.259567	**3.051670**	3.578943
298 K					
q_m	963.7344	963.7598	963.7598	961.1587	963.7598
t	0.894077	0.258769	0.254320	0.791909	0.253838
a_t	1763.1325	7.489999	7.474131	757.0212	7.474152
SSE	**0.000913**	0.002798	0.003144	0.000958	0.003588
SAE	0.073253	**0.049828**	0.081436	0.054779	0.083679
ARE	11.26529	15.39796	**8.014274**	11.95191	8.201007
HYBRID	0.345125	1.031132	0.529987	**0.337681**	0.559546
MPSD	21.51818	30.06426	15.4035	21.99395	**15.19467**
SNE	2.911918	4.375288	3.396264	**2.756885**	3.580662
308 K					
q_m	786.6575	786.5907	786.5907	774.7881	786.5907
t	0.972530	0.298540	0.293919	0.969357	0.292778
a_t	2853.9366	10.20545	10.18921	2809.8128	10.18924
SSE	**0.001023**	0.002681	0.002727	0.001142	0.003559
SAE	0.073209	**0.053488**	0.079509	0.057838	0.084034
ARE	10.34024	15.54552	**8.335307**	10.5874	8.697581
HYBRID	0.33843	1.019661	0.506091	**0.315268**	0.550954
MPSD	18.35504	30.28945	16.06275	18.57913	**15.22843**
SNE	2.761675	4.389806	3.275207	**2.612779**	3.602585

4.5. Temkin isotherm

The sorption data were analysed according to the linear form of the Temkin isotherm and the linear plots are shown in Fig. 4(a) and (b). Examination of the plots reveal that the experimental data of As(III) as well as As(V) are not modelled well across the concentration range studied. However, As(V) provides a better fit to the sorption data as compared to As(III). The R^2 values presented in Table 3 further supports this fact. The linear and non-linear isotherm constants and error analyses for both As(III) and As(V) are presented in Tables 10 and 11, respectively. As is evident from the tables, the isotherm parameters of all the error methods are significantly different from each other as well as from the linearised parameter values. The only parameter set that are somewhat close to those obtained by linearisation are the SSE sets for both As(III) and As(V) at all the three temperatures. It is also interesting to note that in some cases the non-linear parameter sets result in worse errors than the linear set, possibly indicating that the linearisation method in this case has little effect on the error assumptions of least squares. Lastly the HYBRID parameter set produces the best overall fit for both As(III) and As(V) at all temperatures based on the sum of normalised errors.

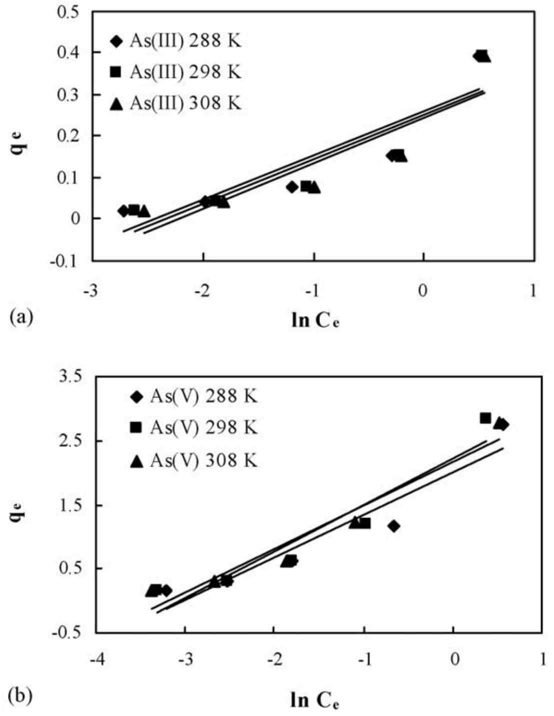

Fig. 4. (a)Temkin isotherms (Eq. (6)) of As(III) sorbed on IOCC; (b) Temkin isotherms (Eq. (12)) of As(V) sorbed on IOCC.

Table 9
Non-linear Toth isotherm parameters for As(V) at temperatures 288, 298 and 308 K

	SSE	SAE	ARE	HYBRID	MPSD
288 K					
q_m	936.6949	936.6949	936.6902	936.6951	936.6949
t	0.179134	0.192731	0.199179	0.181302	0.193839
a_t	2.037734	2.312232	2.452288	2.079489	2.317856
SSE	**0.009835**	0.012992	0.016505	0.009914	0.017931
SAE	0.173792	**0.157824**	0.158105	0.163394	0.248514
ARE	7.459211	6.532313	**6.432941**	6.879799	7.251599
HYBRID	0.585831	0.738354	0.95095	**0.579976**	0.71634
MPSD	13.07202	11.74904	13.14046	12.44193	**11.28701**
SNE	3.858656	3.905914	4.419090	**3.689436**	4.584407
298 K					
q_m	957.5813	957.5811	957.5604	957.5817	957.5811
t	0.184756	0.217357	0.212860	0.201337	0.221851
a_t	2.063894	2.755142	2.649451	2.385319	2.808647
SSE	**0.00821**	0.029196	0.023746	0.01326	0.04291
SAE	0.234226	**0.174051**	0.213838	0.218142	0.330261
ARE	9.796282	5.441583	**4.93676**	6.966695	5.570633
HYBRID	0.727865	0.946835	0.756799	**0.458629**	0.736140
MPSD	17.7626	10.10655	9.001104	10.26194	**7.611848**
SNE	3.669280	3.331865	3.010853	**2.742798**	3.774654
308 K					
q_m	980.8449	980.8443	980.8486	980.8459	980.8443
t	0.140769	0.184054	0.183517	0.161812	0.187934
a_t	1.380439	2.144424	2.074224	1.709995	2.157743
SSE	**0.038413**	0.117738	0.135928	0.0574	0.150903
SAE	0.469247	**0.38602**	0.578303	0.402533	0.614716
ARE	20.2016	11.33646	**10.07493**	12.2331	10.41579
HYBRID	2.964668	3.628818	2.54268	**1.840975**	2.778401
MPSD	36.0183	19.53087	15.25246	20.11133	**15.03950**
SNE	3.834889	3.511603	3.464403	**2.706441**	3.698793

4.6. Linear error analysis

Following the conventional approach of determination of the isotherm parameters by linear regression and judging the best fit isotherm from the R^2 values (Table 3) suggested that the Langmuir isotherm provided a reasonable description and analysis of the experimental data, with the Freundlich isotherm generally producing a close second for As(III) and (V) at all temperatures. However, very surprisingly, the data in Table 12 show that the Freundlich isotherm produced the best fit for both As(III) and As(V) at all the three temperatures based on the measured errors across the range of linear isotherms, with the exception of As(V) at 308 K. The linear parameter set of the Langmuir isotherm provides the second closest fit over all the error methods for both As(III) and As(V) at all temperatures excepting 308 K for As(V) for which the reverse is true. However, a plot of q_e versus C_e (not shown here) at all the three temperatures show that the Freundlich isotherm provides a better fit at the higher end of the concentration range compared to Langmuir isotherm.

Excepting the Langmuir and Freundlich isotherms, the sum of normalised error values of the linear isotherms appear to give a reasonable indication of the quality of the linear isotherm fit based on the R^2 values. The anomaly in the Langmuir isotherm results based on SNE values and R^2 values may be due to the fact that linearisation of the Langmuir isotherm do not require taking logarithms. For the Freundlich isotherm, linearisation requires taking logarithms, introducing similar effects to the error structure. In addition to this, taking logarithms also leads to better fits at the extremes of concentrations since linear regression implicitly minimises the sum of squares of the errors to determine the equation parameters. Thus the error in a value of 10^3 will have a similar weighting to the error in the value of 10^{-3} [11].

4.7. Non-linear error analysis

The conventional method of selection of the best-fit isotherm based on the regression coefficient is not always the appropriate method for choosing a model for the sorption equilibria. Based on any of the error measures, better fits can be obtained for any isotherm by using non-linear isotherm.

In the present study, based on the absolute error values, the quality of the isotherm fit can be arranged in order of increasing weightage of the errors as: Freundlich < Toth < Langmuir < D–R < Temkin for As(III) and Langmuir < Toth < Freundlich < D–R < Temkin for As(V). From this it is evident that Freundlich isotherm provides the best fit for As(III) sorption at equilibrium, contrary to the Langmuir isotherm obtained from the regression coefficient values of linear analysis. Moreover, compared to other isotherms, the parameter sets of the Freundlich isotherm for both As(III) and (V) were remarkably

Table 10
Linear and non-linear Temkin isotherm parameters for As(III) at temperatures 288, 298 and 308 K

	LTFM	SSE	SAE	ARE	HYBRID	MPSD
288 K						
B_1	0.1068	0.106848	0.071963	0.039599	0.070049	0.047640
K_T	11.36697	11.35495	11.38164	25.00649	16.92509	21.93084
SSE	0.017522	**0.017522**	0.035686	0.062951	0.028396	0.050924
SAE	0.264322	0.264265	**0.242569**	0.293294	0.248914	0.2681
ARE	78.73866	78.8038	55.63839	**20.85707**	39.68029	23.7858
HYBRID	6.996918	7.013808	5.612186	5.539229	**3.286796**	4.475816
MPSD	150.1213	150.4444	118.2795	40.11099	54.23337	**37.94686**
SNE	4.174175	4.179368	3.686336	3.321048	**2.632404**	2.915258
298 K						
B_1	0.1081	0.108088	0.073066	0.039331	0.069313	0.046617
K_T	10.19527	10.19894	10.20980	21.33648	15.33104	19.97937
SSE	0.018617	**0.018616**	0.036222	0.065446	0.030306	0.053379
SAE	0.272884	0.272909	**0.249163**	0.301061	0.253496	0.277132
ARE	82.21952	82.20133	58.31427	**22.79454**	40.37829	24.67071
HYBRID	7.558496	7.553173	5.842263	5.799814	**3.506544**	4.724597
MPSD	156.3304	156.2238	122.1475	41.27536	55.56008	**38.96699**
SNE	4.190871	4.189332	3.644613	3.308590	**2.615504**	2.910527
308 K						
B_1	0.11	0.110001	0.069333	0.038443	0.069494	0.046144
K_T	9.393331	9.388932	11.01720	20.19915	14.15061	18.53021
SSE	0.019048	**0.019046**	0.036812	0.067635	0.031329	0.055166
SAE	0.277464	0.277414	**0.238084**	0.307509	0.255704	0.283684
ARE	85.16384	85.17433	44.25268	**23.05173**	41.20519	25.43725
HYBRID	7.936039	7.941151	4.626282	6.031571	**3.642697**	4.910074
MPSD	161.3880	161.5128	90.57381	42.16758	57.05143	**39.90339**
SNE	4.182385	4.183733	2.981418	3.291254	**2.590458**	2.902183

Table 11
Linear and non-linear Temkin isotherm parameters for As(V) at temperatures 288, 298 and 308 K

	LTFM	SSE	SAE	ARE	HYBRID	MPSD
288 K						
B_1	0.6663	0.666259	0.461280	0.323774	0.499947	0.364970
K_T	20.52743	20.53108	23.77581	40.00323	28.84400	36.18898
SSE	0.430686	**0.430685**	1.095382	1.928628	0.711469	1.547365
SAE	1.299359	1.29945	**1.233807**	1.626697	1.351224	1.46996
ARE	55.52689	55.51968	31.56822	**17.95548**	32.84444	19.77926
HYBRID	26.57364	26.56094	19.68853	24.40635	**13.12672**	19.71314
MPSD	111.2477	111.2041	69.92712	33.15934	45.24946	**31.77645**
SNE	4.022084	4.021139	3.26443	3.539875	**2.691779**	3.089639
298 K						
B_1	0.7311	0.731078	0.588825	0.301613	0.520673	0.348014
K_T	21.22088	21.22148	21.21835	46.38627	30.80364	40.81227
SSE	0.440690	**0.440689**	0.805388	2.619836	0.853523	2.119554
SAE	1.391107	1.391113	**1.291399**	2.006467	1.43777	1.853283
ARE	67.83469	67.83161	50.74321	**22.34919**	38.3052	26.16349
HYBRID	36.36450	36.3604	30.07292	33.20887	**16.87414**	27.0046
MPSD	136.0069	135.9973	118.7176	39.40743	55.74727	**37.87705**
SNE	3.861525	3.861298	3.398945	3.532434	**2.480959**	3.139493
308 K						
B_1	0.6824	0.682362	0.768574	0.304593	0.521838	0.370949
K_T	24.17281	24.17601	21.63308	48.95921	33.34426	42.40676
SSE	0.260829	**0.260828**	0.337825	2.164521	0.521192	1.469999
SAE	1.047509	1.047585	**1.001404**	1.853868	1.151479	1.609547
ARE	53.91001	53.90386	65.49434	**20.25735**	32.71553	23.26597
HYBRID	24.19552	24.18563	40.4911	28.50703	**11.80327**	19.65861
MPSD	111.4477	111.4145	149.0223	36.24328	48.43618	**33.37034**
SNE	3.106218	3.105622	4.033394	3.338536	**2.08754**	2.687511

Table 12
Comparison of linear isotherms based on the sum of normalised errors (SNE)[a]

Linear isother	As(III)			As(V)		
	288 K	298 K	308 K	288 K	298 K	308 K
Langmuir	1.107804	1.272078	1.386343	1.147376	0.776355	**0.367143**
Freundlich	**0.494544**	**0.53702**	**0.544601**	**0.629902**	**0.709933**	1.90784
Dubinin–Radushkevich	3.087451	3.098382	3.082382	3.114076	2.912842	2.977398
Temkin	4.567477	4.563639	4.558052	4.475848	4.502381	4.384305

[a] Denotes normalised errors across linear isotherm range (instead of error functions).

consistent and quite similar to the linear transform values. In certain cases it has been found that the parameters obtained by linearization are better than the values derived by non-linear regression, particularly in cases when the parameter are inconsistent and vary widely as in the case of Langmuir isotherm.

The HYBRID error measure produced the parameter set providing the lowest sum of normalised errors in 17 out of 24 systems (examining four isotherms for each of the states of arsenic at all the three temperatures), for all the four two-parameter isotherms examined. The SAE error measure was the second best for 11 of the 24 systems. For the three parameter Toth isotherm, the HYBRID error measure produced the parameter set that gave the lowest sum of normalised errors in four out of six systems. The Toth isotherm was found to provide the second best fit to the experimental data for both As(III) and As(V).

5. Conclusions

A detailed study has been carried out to determine the best isotherm models for the equilibrium adsorption of arsenic (III and V) onto IOCC at three different temperatures. From the values of the linear isotherm parameters, it can be concluded that the adsorption process for arsenic onto IOCC is a temperature dependent phenomena with As(III) exhibiting an exothermic nature of adsorption and As(V) exhibiting endothermic nature of adsorption.

Considering the results presented for all the isotherms, the following conclusions can be drawn:

- Excepting the values of linear coefficients of determination, all other analyses indicated Freundlich isotherm as the best-fit isotherm for arsenic sorption in linear as well as non-linear systems irrespective of the temperature.
- Excepting the Langmuir isotherm, the order of the linear regression coefficients was able to provide a good indication of the relative ranking of the linear isotherm fits based on the sum of normalised errors.
- Excepting the Freundlich and Toth isotherms, the non-linear derived parameters were not able to produce reasonable estimates of the values derived by linear regression.
- The Toth isotherm was found to be the second best-fit isotherm for the arsenic equilibrium data at all temperatures.
- In the non-linear regression analysis, the Langmuir isotherm produced very inconsistent results quite different from that obtained by linear regression from which it can be inferred that it is not a particularly very good model for arsenic sorption.
- The HYBRID error function appeared to produce the best fit isotherm parameter values for the two as well as three parameter isotherms.

A detailed study on the linear and non-linear regression gave different models as the best fitting isotherm for the given data set, thus indicating a significant difference between the analytical methods. Therefore, to ensure better results, it is necessary that the data set be evaluated by both linear and non-linear regression analyses.

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