Electronic Supplementary Material (ESI) for RSC Advances.

Synthesis of nano zirconia

$ZrOCl_2.8H_2O$ was weighed according to make a 0.075 M solution. Afterwards, $ZrOCl_2$ solution was precipitated with NH_4OH (25%) with continuous stirring on a magnetic stirrer till the pH raises in the range of 10 to 10.5.This resulted in the formation of precipitate of Zirconium Hydroxide. The precipitate was filtered and washed with distilled water until traces of chloride were completely removed from the filtrate. Complete removal of chloride from filtrate was checked by titrating it with $AgNO_3$ using potassium chromate as indicator. Zirconium hydroxide, so formed was dried in oven at 80 – 90 ^{0}C for 24 h. Afterwards; it was calcined at 600^{o}C for 3 h.

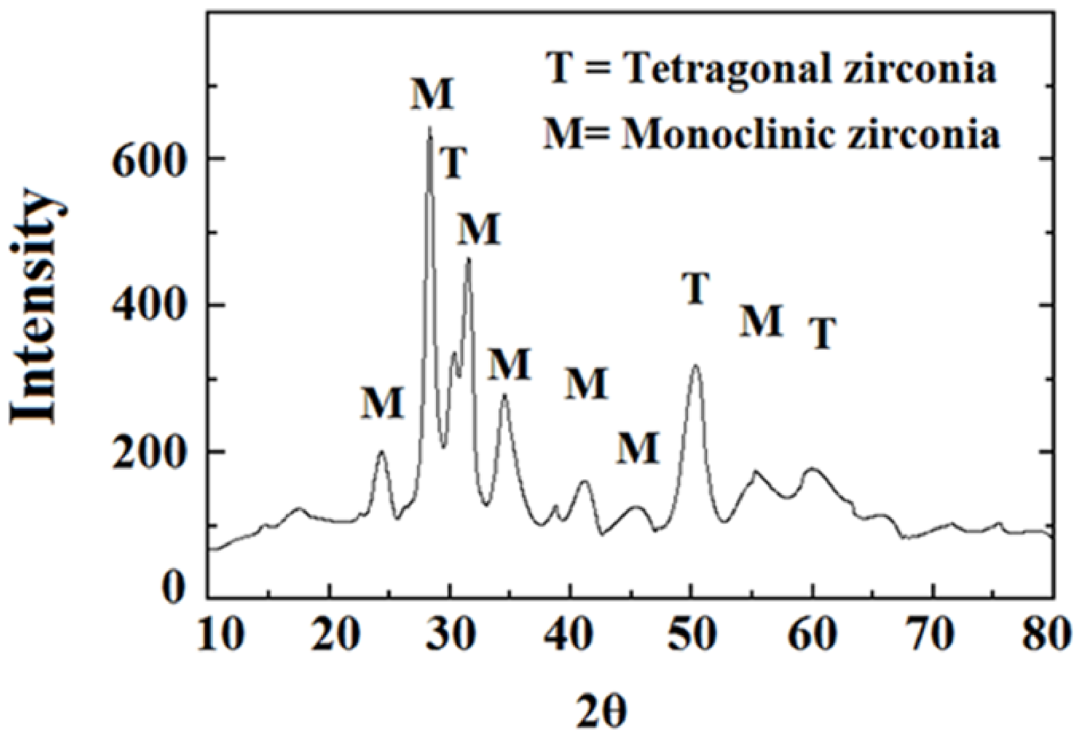

Figure 1A. XRD of nano zirconia

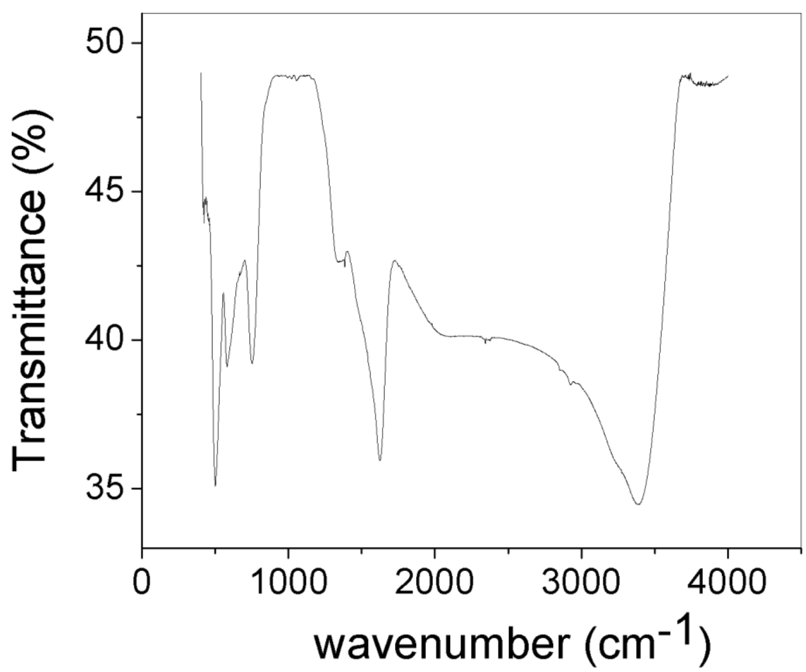

Figure 2A. FTIR of nano zirconia

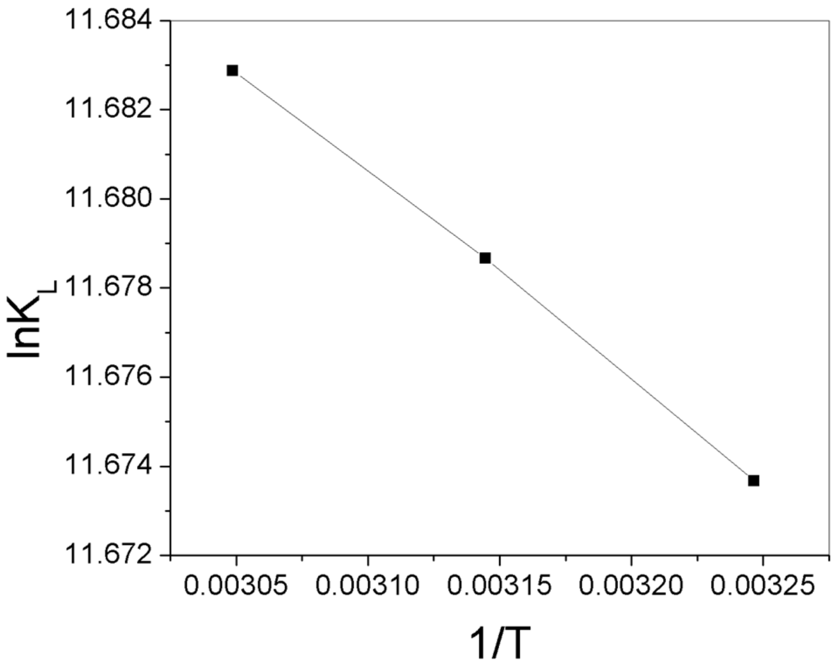

Fig 3A Plot of ln KL against 1/T using linear Langmuir adsorption parameter for the adsorption of orange on nano zirconia

.

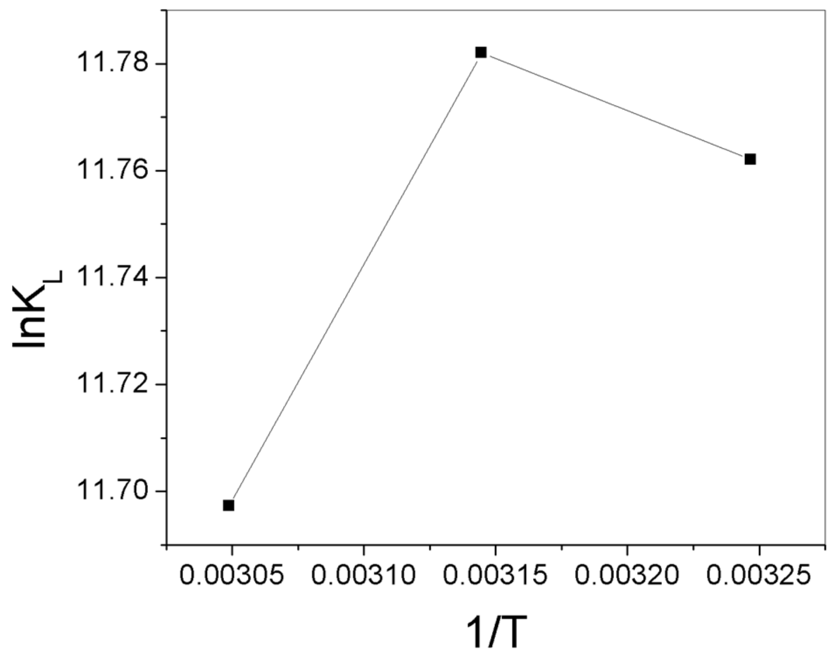

Fig 4A Plot of ln K_L against 1/T using non linear Langmuir adsorption parameter for the adsorption of orange on nano zirconia

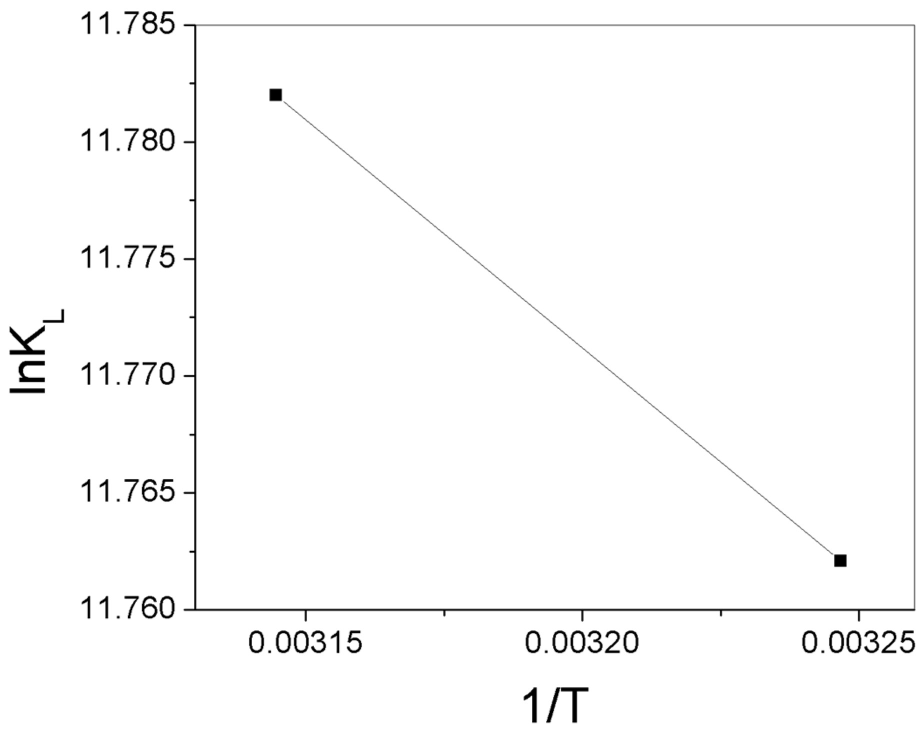

Fig 5A Plot of ln K_L against 1/T using non linear Langmuir adsorption parameter at 308K and 318K for the adsorption of orange on nano zirconia

A brief discussion error function used and their determination are as follows[1]:

The sum of the square of the errors (ERRSQ)

The sum of the squares of the errors method equation can be represented as follows:

$$\sum_{i=1}^{n} (q_{e,\,i,\,calc} - q_{e,i,meas})^2 \quad (1)$$

Here $q_{e,i,calc}$ are the theoretical adsorbed solid phase concentrations of adsorbate on adsorbent, which have been calculated from isotherm equation and $q_{e,i,meas}$ are the experimentally determined adsorbed adsorbate concentration obtained from equation. Despite its extended use, function has a significant shortcoming i.e. isotherm parameters calculated from such error functions provided a better fit at higher adsorbate concentration range. The chief reason for this is as concentration increases, magnitude of errors also increases and hence square of the errors.

Hybrid fractional error function (HYBRID)

HYBRID error function was developed in order to ameliorate sum of squares of the errors at low concentrations by dividing it by measured values. It also comprises the number of degrees of freedom of the system (i.e. the number of data points) and number of parameters of the isotherm equation as a divisor.

$$\frac{100}{n-p}\sum_{i=1}^{n} \frac{(q_{e,i,meas} - q_{e,\,i,\,calc})^2}{q_{e,i,meas}} \quad (2)$$

Here n is the degree of freedom and p is the number of parameters.

Marquardt's percent standard deviation (MPSD)

This error function is similar in some respect to geometric mean error distribution and has been modified according to number of degrees of freedom of the system:

$$100\sqrt{\frac{1}{n-p}\sum_{i=1}^{n}\frac{(q_{e,i,meas}-q_{e,i,calc})^2}{q_{e,i,meas}}} \qquad (3)$$

The average relative error (ARE)

This error function attempts to depreciate the fractional error distribution across the overall concentration range.

$$\frac{100}{n}\sum_{i=1}^{n}\left|\frac{q_{e,i,calc}-q_{e,i,meas}}{q_{e,i,meas}}\right| \qquad (4)$$

The sum of the absolute errors (EABS)

This approach is analogous to the sum of the squares of the errors. Isotherm parameters procured employing this error function furnish a better fit as extent of the error increases, biasing the fit towards the higher concentration data.

$$\sum_{i=1}^{n}\left|q_{e,i,calc}-q_{e,i,meas}\right| \qquad (5)$$

In addition to above error function used coefficient of determination is also used for its for their eligibility to predict best fit isotherm and kinetic model.

Coefficient of determination

Percentage variability in the dependent variable is represented by the coefficient of determination. The value of the coefficient of determination varied from 0 to 1.

$$r^2 = S^2/\ S_{(XX)}\ S_{(YY)} \qquad (6)$$

Here $S_{(XY)}$ is the sum of squares of X and Y, $S_{(XX)}$ is the sum of the squares of X and S (YY) is the sum of squares of Y.

Langmuir isotherm parameters, Freundlich isotherm parameters, pseudo first order kinetic and pseudo second order kinetic parameters determined by different error functions for removal of orange G by nano zirconia are represented in following Tables

Table 1 A. Langmuir isotherm parameters determined by different error functions for removal of orange G by nano zirconia

35 DEGREE	**LTFM**	**ERRSQ**	**HYBRID**	**MPSD**	**ARE**	**EABS**
Q	47.2143	46.02241	46.65564	26.12031	26.34896	38.75597
b	0.259686	0.315935	0.283638	0.549974	0.541355	0.518234
Coefficient of determination (r^2)	0.9600	0.9661	0.9660	0.4753	0.4775	0.7499
ERRSQ	33.0953949	25.06405	27.49303	1107.183	1083.395	128.4707
HYBRID	29.02200916	30.1292	26.92769	704.6451	689.8078	116.5946
MPSD	23.45598295	24.76613	23.98151	95.64338	94.6728	44.87172
ARE	7.818660985	8.255377	7.993837	31.88113	31.5576	14.95724
EABS	12.74403396	11.53077	12.18144	71.4371	70.68603	23.89889
Sum of normalized error	0.739961804	0.744692	0.735044	5	4.926649	1.554357
45 DEGREE	LTFM	ERRSQ	HYBRID	MPSD	ARE	EABS
Q	47.7326	47.09744	47.09744	47.79595	26.34658	45.95895
B	0.2609616	0.289395	0.289395	0.220885	0.541454	0.351928
Coefficient of determination (r^2)	0.9828	0.9843	0.9838	0.9647	0.4741	0.9707
ERRSQ	14.46909117	12.29345	13.64668	33.5349	1131.844	19.88046
HYBRID	16.26694555	17.88781	16.11952	31.43813	710.033	36.8201
MPSD	17.65778761	18.46986	17.83182	16.27042	95.33198	20.37318

ARE	5.885929202	6.156619	5.943939	5.423473	31.77733	6.791059
EABS	8.180172847	7.640775	8.071762	9.092869	72.02283	6.723899
Sum of normalized error	0.51971963	0.529628	0.520931	0.541498	5	0.590195
55 DEGREE	LTFM	ERRSQ	HYBRID	MPSD	ARE	EABS
Q	54.2593	53.7945	54.31359	53.85903	25.12505	53.3989
b	0.2620876	0.280489	0.265869	0.283281	6.032301	0.295822
Coefficient of determination (r^2)	0.9933	0.9942	0.9938	0.9941	0.3023	0.9933
ERRSQ	7.473986779	6.205658	6.886651	6.311468	1682.21	6.936953
HYBRID	6.804120753	7.429003	6.639615	7.947963	1065.648	9.985891
MPSD	11.63096184	11.51778	11.34705	11.2946	127.0975	11.57555
ARE	3.876987279	3.839261	3.782351	3.764866	42.36584	3.858516
EABS	6.206484477	5.375205	5.779218	5.043227	86.14038	4.827222
Sum of normalized error	0.265902953	0.254304	0.255972	0.247488	5	0.251686

Table 1B. Freundlich isotherm parameters determined by different error functions for removal of orange G by nano zirconia

35 DEGREE	LTFM	ERRSQ	HYBRID	MPSD	ARE	EABS
K	13.85	1.004178	0.991707	1	1	1
n	3.14	1.046043	0.993533	1	1	1
Coefficient of determination (r^2)	0.5330	0.6592	0.6650	0.6652	0.6652	0.6652
ERRSQ	71667.69059	1693.793	1702.36	1703.205	1703.205	1703.205
HYBRID	41066.38357	1484.405	1479.449	1479.461	1479.461	1479.461
MPSD	543.9439113	164.3416	162.9233	162.855	162.855	162.855
ARE	181.3146371	54.78055	54.30776	54.28501	54.28501	54.28501
EABS	442.8912648	88.16704	87.53063	87.5	87.5	87.5
Sum of normalized error	5	0.863112	0.856458	0.666831	1.547708	1.547708
45 DEGREE	LTFM	ERRSQ	HYBRID	MPSD	ARE	EABS
K	14.3	0.996417	0.998177	1.043401	1.043261	1.042973
n	3.21	1.005479	0.967473	0.956451	0.956323	0.956059
Coefficient of determination (r^2)	0.5325	0.6590	0.6650	0.6712	0.6712	0.6712
ERRSQ	73463.4943	1732.842	1742.169	1788.921	1788.921	1788.921
HYBRID	42093.77949	1496.231	1490.902	1502.139	1502.139	1502.139
MPSD	549.3700756	168.8045	167.5217	165.659	165.659	165.659
ARE	183.1233585	56.26816	55.84057	55.21967	55.21967	55.21967
EABS	447.8675271	92.53142	91.98567	91.19318	91.19318	91.19318
Sum of normalized error	5	0.880276	0.874388	0.86674	0.86674	0.86674

55 DEGREE	LTFM	ERRSQ	HYBRID	MPSD	ARE	EABS
K	14.53	1.126694	1.096858	1.2	1.2	1.2
n	2.76	0.830583	0.770102	0.8	0.8	0.8
Coefficient of determination (r^2)	0.5262	0.6694	0.6768	0.6825	0.6825	0.6825
ERRSQ	110569.8242	2014.681	2030.954	2087.585	2087.585	2087.585
HYBRID	63348.48608	1602.58	1594.249	1604.636	1604.636	1604.636
MPSD	654.9675977	170.8229	169.3647	167.7366	167.7366	167.7366
ARE	218.3225326	56.94096	56.45491	55.91219	55.91219	55.91219
EABS	543.3553313	99.79174	99.32769	98.80953	98.80953	98.80952
Sum of normalized error	5	0.748799	0.743509	0.738259	0.738259	0.738259

Table 2 A. Pseudo first order kinetic parameters determined by different error functions for removal of Orange G by nano zirconia

25 ppm	LTFM	ERRSQ	HYBRID	MPSD	ARE	EABS
K1	0.03015	0.425803	0.426821359	0.429314229	0.42931724	0.429315294
Coefficient of determination (r^2)	0.5344	0.8059	0.8041	0.8000	0.8000	0.8000
ERRSQ	146.5678	0.382054	0.382250299	0.382586415	0.382587011	0.382586333
HYBRID	276.0217	0.673252	0.672909971	0.67343663	0.673438073	0.673437551
MPSD	103.0262	4.718345	4.664238651	4.591574339	4.591471494	4.591445296
ARE	32.91052	1.50722	1.489936384	1.466724621	1.466691768	1.466683399
EABS	24.97338	1.201645	1.188615413	1.172188554	1.172164393	1.172156534
Sum of normalized error	5	0.144758	0.143185878	0.141121707	0.141118752	0.141117922
50 ppm	LTFM	ERRSQ	HYBRID	MPSD	ARE	EABS
K1	0.04219	0.425803	0.268503051	0.276351828	0.274740679	0.268845556
Coefficient of determination (r^2)	0.6077	0.4938	0.8668	0.8550	0.8561	0.8546
ERRSQ	286.2516	780.1634	4.484169376	4.634436875	4.709047727	5.230203955
HYBRID	308.2615	704.2209	4.263869143	4.429271325	4.519332075	5.05758351
MPSD	74.02132	149.2769	8.779638715	7.858995199	7.860484692	7.913590772
ARE	23.64524	47.68475	2.804552712	2.510463929	2.51093973	2.527903845
EABS	32.19071	72.91813	4.19125323	3.802087805	3.792005893	3.776352561
Sum of normalized error	2.237842	5	0.186910269	0.169666023	0.169771238	0.17170041

75 ppm	LTFM	ERRSQ	HYBRID	MPSD	ARE	EABS
K1	0.02266	0.196366	0.204921452	0.231004551	0.229317373	0.219358095
Coefficient of determination (r^2)	0.5952	0.8383	0.8235	0.7555	0.7637	0.7940
ERRSQ	981.4869	24.97384	25.23071226	28.78072615	28.05651969	27.33445293
HYBRID	729.3619	16.58036	16.38499033	17.93295182	17.62595011	17.97494295
MPSD	111.6674	16.07249	15.55082857	13.98901587	13.99756321	14.07405856
ARE	35.67085	5.134167	4.96752997	4.468627202	4.471357551	4.495793095
EABS	70.44231	10.80856	10.64366826	10.11026781	10.07747874	9.887219641
Sum of normalized error	5	0.489479	0.477789512	0.447984104	0.446512931	0.444924871
100 ppm	LTFM	ERRSQ	HYBRID	MPSD	ARE	EABS
K1	0.00859	0.182294	0.198872365	0.240814289	0.240790005	0.229719237
Coefficient of determination (r^2)	0.5421	0.5807	0.5294	0.4007	0.4007	0.4316
ERRSQ	2878.193	142.6295	145.1274312	179.2844313	179.2814516	159.6377727
HYBRID	1735.308	66.73113	65.27067471	76.34960909	76.34801242	69.05617571
MPSD	182.8151	28.10178	25.46829432	20.75242809	20.74966641	21.00599305
ARE	58.39815	8.976784	8.135548196	6.629119986	6.628237802	6.710118341
EABS	138.4629	23.77728	22.25522913	19.84461032	19.84296791	19.62907177
Sum of normalized error	5	0.567167	0.527390585	0.476641018	0.476596988	0.466829369

Table 2 B. Pseudo second order kinetic parameters determined by different error functions for removal of Orange G by nano zirconia

25 ppm	**LTFM**	**ERRSQ**	**HYBRID**	**MPSD**	**ARE**	**EABS**
K2	0.0632	0.104054	0.104712931	0.113284941	0.113341612	0.113792691
Coefficient of determination (r^2)	0.8445	0.9647	0.9643	0.9511	0.9510	0.9484
ERRSQ	0.837593	0.068935	0.068993398	0.083937138	0.083905679	0.088282524
HYBRID	1.63299	0.120252	0.12014409	0.143820946	0.143778106	0.125846977
MPSD	6.406205	2.580317	2.332221668	2.172671575	2.172250392	2.002399311
ARE	2.046387	0.824252	0.816107579	0.694034476	0.693899934	0.700693796
EABS	1.525857	0.655419	0.649783258	0.562233266	0.562202772	0.567992321
SUM of normalized error	5	1.391051	1.344653084	1.235057305	1.234842035	1.209687681
50 ppm	LTFM	ERRSQ	HYBRID	MPSD	ARE	EABS
K2	0.0191	0.020571	0.020735649	0.021128707	0.026458451	0.021135236
Coefficient of determination (r^2)	0.9559	0.9918	0.9917	0.9894	0.9510	0.9484
ERRSQ	1.681728	0.263618	0.264648759	0.328786471	0.083905679	0.088282524
HYBRID	1.684305	0.261262	0.260150402	0.32076915	0.143778106	0.125846977
MPSD	6.608986	2.106351	2.098515713	1.711763933	2.172250392	2.002399311
ARE	2.111163	0.672849	0.670346255	0.546802931	0.693899934	0.700693796
EABS	3.080551	0.96068	0.965456236	0.804508694	0.562202772	0.567992321
SUM of normalized error	5	1.261143	1.260275728	1.165119569	0.975119365	0.946473378

75 ppm	LTFM	ERRSQ	HYBRID	MPSD	ARE	EABS
K2	0.0046	0.008616	0.008900904	0.009830476	2.468707204	0.008707777
Coefficient of determination (r^2)	0.8507	0.9641	0.9623	0.9513	0.0736	0.9517
ERRSQ	47.93053	4.878509	4.930737423	5.687569039	140.5887361	5.364108351
HYBRID	39.61056	3.146157	3.106122441	3.490217136	116.66297	2.848635351
MPSD	22.31025	6.772004	6.587762526	5.904315614	36.02872539	6.457375614
ARE	7.126748	2.163237	2.104383547	1.886064439	11.50895416	2.259610762
EABS	13.35967	4.558743	4.507536736	4.270569521	21.32192836	4.772668233
Sum of normalized error	2.545496	0.651396	0.638795628	0.598418494	5	0.661974302
100 ppm	LTFM	ERRSQ	HYBRID	MPSD	ARE	EABS
K2	0.0017	0.005853	0.006789161	1.969560643	0.009847067	2.396393443
Coefficient of determination (r^2)	0.7693	0.7173	0.6757	0.0008	0.5198	0.0008
ERRSQ	209.7305	91.28155	93.2508094	297.796103	125.6090223	298.2040355
HYBRID	143.5291	42.32472	41.15624485	170.1815913	52.04626802	142.0754665
MPSD	45.06368	23.17874	20.25525817	41.07319114	13.35409133	37.52978851
ARE	14.39506	7.404178	6.470304882	13.12034963	4.265807999	13.13269029
EABS	32.31578	19.83093	17.9507428	31.41398185	13.62390906	31.43772027
Sum of normalized error	4.5467	2.197179	2.008986161	4.793622013	1.741309654	4.552797089

References

1. L. S. Chan, W. H. Cheung, S. J. Allen and G. McKay, *Chinese Journal of Chemical Engineering*, 2012, **20**, 535-542.