Studies on Pb(II) and Cd(II) adsorption by Fe(II) and Fe(III) silicate precipitation tubes in aqueous medium

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Abstract : Adsorption of Pb(II) and Cd(II) on Fe(II) and Fe(III) silicate precipitation tubes (Fe^{II}SPT and Fe^{III}SPT) in aqueous medium has been studied and reported. Fe^{III}SPT is a better adsorbent than Fe^{II}SPT with reference to Pb(II) and Cd(II). Adsorption varies nonlinearly with initial concentration and adsorbent dose. Experimental adsorption data are modeled with Langmuir and Freundlich isotherms and isotherm parameters are obtained through regression of linearized isotherm equations as well as through direct and robust optimization of parent equations. Robust optimization always yields better fits as opposed to linear regression in terms of Sum Square Error (SSE) and goodness of the fit (R^2) between experimental and optimized model data. Pb(II) adsorption on both Fe^{II}SPT and Fe^{III}SPT and Cd(II) adsorption on Fe^{II}SPT may be better represented by Freundlich isotherm while Cd(II) adsorption on Fe^{III}SPT is more amenable to Langmuir form. Modifications to traditional Langmuir and Freundlich isotherms are proposed in which initial adsorbate concentration is introduced into the original form. The fit of experimental data into the modified Langmuir form is remarkable. Both Fe^{II}SPT and Fe^{III}SPT are identified with very high Pb(II) and Cd(II) loading capacities.

Keywords : Adsorption, Lead, Cadimum, Iron, Precipitation, Robust optimization.

INTRODUCTION

Growth of self assembled hollow tree like structures emanating from the reaction between some metal salts and sodium silicate is popularly known as 'silica garden' reaction. These tubular structures are also called metal silicate precipitation tubes. Metal silicate precipitation tubes produced through 'silica garden route' is a genre of compounds known from an early date but not really looked upon seriously from an application perspective though there has been some advancement in this direction in recent times. Adsorption of heavy metal ions in aqueous medium is one such area where these compounds have shown some promise[1-5].

Historically first reporting of 'silica garden' reaction may be credited to Glauber about 350 years back when he observed growth of tree like structures during a reaction between FeCl$_2$ and K$_2$SiO$_3$ [6]. Since then a number of metal ions have been reported to exhibit 'silica garden' reaction that include Ca(II) [3], Fe(III) [4], Fe(II) [5,6], Co(II) [7,8], Al(III) [9], Cu(II), Ni(II), Mn(II), Mg(II) and Zn(II) [10-11].

Though first 'silica garden' reaction was carried out with Fe(II) salts, inexplicably Fe(III) salts were kept out of the ambit of this reaction till recently. Fe(II) and Fe(III) silicate precipitation tubes produced through silica garden route have been characterized in detail and broadly assessed for their heavy metal adsorption capability in aqueous medium[5].

This communication aims to report in detail studies on Pb(II) and Cd(II) adsorption by Fe(II) and Fe(III) silicate precipitation tubes in aqueous medium.

MATERIALS AND METHODS

Adsorbent [Fe(II) and Fe(III) silicate precipitation tubes]

Fe(II) and Fe(III) Silicate Precipitation Tube, hereafter to be called as Fe^{II}SPT and Fe^{III}SPT respectively, were synthesized in the laboratory.

Adsorbate [Pb(II), Cd(II)]

AR grade $Pb(NO_3)_2$ and $CdCl_2$ were used for making Pb(II) and Cd(II) solutions. Solutions were prepared from 1000 mgl^{-1} stock through serial dilution as appropriate. 18M ASTM Grade 1 water was used for making the solutions.

Instrumental

GBC AVANTA atomic absorption spectrometer fitted with an air acetylene burner was used for metal ion measurement in aqueous medium.

Adsorption experiments

All adsorption experiments with Pb(II) and Cd(II) were carried out in batches in stoppered conical flasks containing 50 ml of heavy metal ion solution of desired strength (initial concentration, C_0), pH and known weight of 'as synthesized' Fe^{II}SPT or Fe^{III}SPT. Contents were shaken in a horizontal shaker for a definite period of time for intimate contact. The contact time was maintained at 30 min. which was sufficient for attaining adsorption equilibrium in the working concentration range.

Adsorption envelopes of Pb(II) and Cd(II) on the Fe^{II}SPT and Fe^{III}SPT surface were developed in the pH range of 2.0-7.0 and 2.0-9.0 respectively. Dilute NaOH and HCl were used for making pH adjustments.

Pb(II) and Cd(II) adsorption isotherms on Fe^{II}SPT and Fe^{III}SPT surface were developed at 0.01 g adsorbent weight.

RESULTS AND DISCUSSION

Characterization of Fe^{II}SPT and Fe^{III}SPT

Fe^{II}SPT and Fe^{III}SPT were characterized earlier in detail. Only the salient features of these products will be mentioned here while the details may be found elsewhere[4-5].

Fe^{II}SPT fibres were fine bristle like, off white in colour that slowly turned into light green while those of Fe^{III}SPT were thick and orange coloured that changed to dark brown. Both microtubes were hierarchically built from smaller nano tubules of 5-10 nm diameters. Figs. 1a and b show SEM images of Fe^{II}SPT and Fe^{III}SPT microtubes. 'As synthesized' Fe^{II}SPT was partly crystalline and partly amorphous while Fe^{III}SPT was fully amorphous. Both turned crystalline on heating at 900°C. Morphology and chemical compositions at the exterior and interior surface of both the products were different. BET surface area of Fe^{II}SPT was four times more than that of Fe^{III}SPT. Isoelectric point in both was well below pH 6 and between the two it was lower in Fe^{III}SPT. These tubes were finely crushed before using as adsorbent.
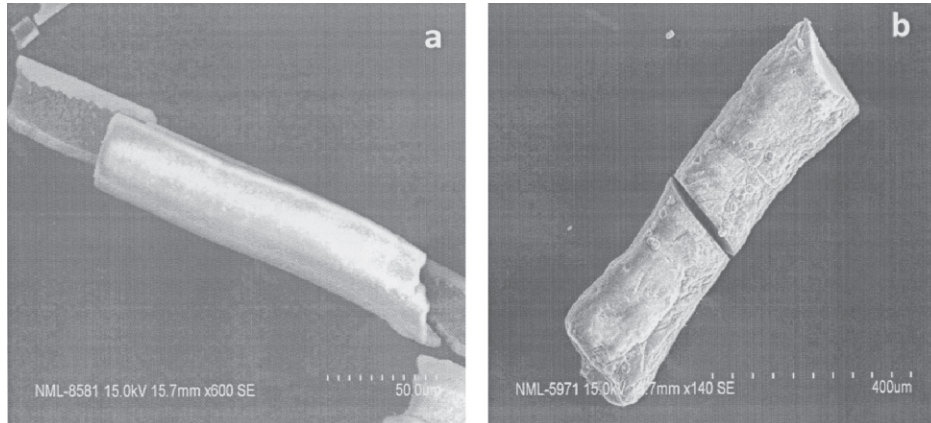
Figs. : 1a and b

*Adsorption screening of heavy metals with Fe^{II}SPT and Fe^{III}SPT*

'As synthesized' Fe^{II}SPT and Fe^{III}SPT were assessed as adsorbents with reference to a number of heavy metal ions in aqueous medium[5], based on which, Pb(II) and Cd(II) were chosen for detailed investigation as adsorbate in the present study.

Contact time

Preliminary batch adsorption experiments were carried out to ascertain the time needed for attaining adsorption equilibrium in the studied concentration range and 30 min. was found sufficient for this purpose.

*Effect of initial Pb(II) and Cd(II) concentration*

The dependence of Pb(II) and Cd(II) uptake on initial adsorbate concentration C_0 by 0.01 g of Fe^{II}SPT and Fe^{III}SPT has been shown in Figs. 2a and b. Metal ion uptake has been plotted along Y-axis, while X-axis plots initial metal ion concentration, C_0. It is apparent that metal ion uptake by both the adsorbents increases in a non-linear manner with increase in initial metal ion concentration and prima facie, Fe^{III}SPT is a better adsorbent than Fe$_{II}$SPT with reference to both Pb(II) and Cd(II). It may be appropriate to mention at this stage that BET surface area of Fe^{III}SPT was four times higher and IEP was lower than that of Fe^{II}SPT. Both these facts indicate that Fe^{III}SPT could be a better adsorbent than Fe^{II}SPT with reference to heavy metal ions.
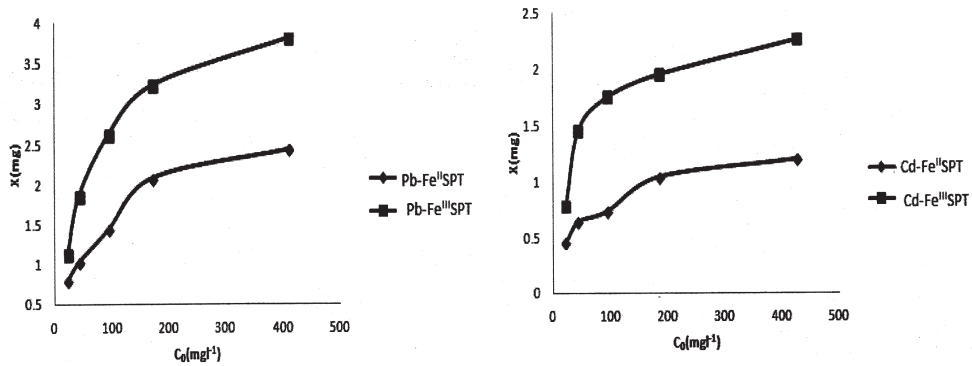
Figs. : 2a-b

Effect of pH

Figs. 3a and b show the effect of pH on Pb(II) and Cd(II) adsorption on $Fe^{II}SPT$ and $Fe^{III}SPT$. It is readily apparent from Figs. 3a and 3b that metal adsorption increases with increase in pH up to 7 for Pb(II) and 9 for Cd(II). Beyond this precipitation of the corresponding metal ion takes place.
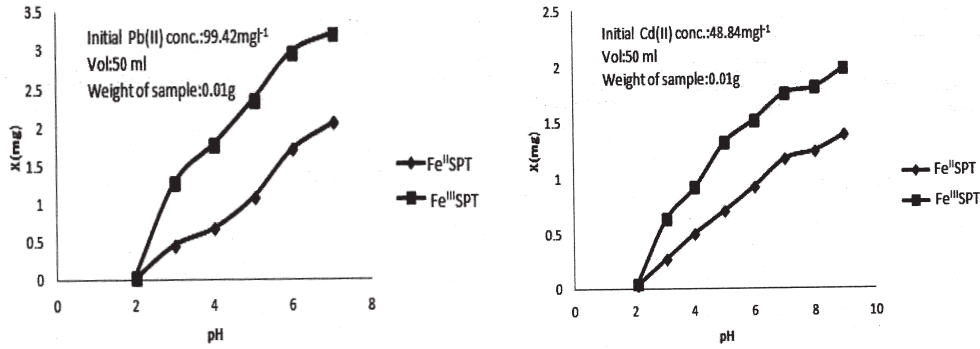
Figs. 3a-b

Adsorption isotherm

Experimental adsorption data were modeled with commonly used Langmuir and Freundlich isotherms, expressions for which have been shown in Table 1.

Table 1 : Conventional Langmuir and Freundlich forms along with their modified versions

Isotherm	Conventional	Transformed	
Langmuir	$\dfrac{X}{m} = \dfrac{b^V_m C_e}{1+bC_e}$	$\dfrac{X}{m} = \dfrac{pqC_e}{1+pC_e}$ $p=b,\ q=V_m$	...(1)
Freundlich	$\dfrac{X}{m} = k_f . C_e^{1/n}$	$\dfrac{X}{m} = p\,C_e^{\,q}$ $p=k_f,\ q=1/n$	...(2)
Langmuir (Linearized)	$\dfrac{X}{m} = \dfrac{1}{V_m C_e} + \dfrac{1}{V_m}$	$\dfrac{X}{m} = \dfrac{1}{p.qC_e} + \dfrac{1}{q}$ $p=b,\ q=V_m$	...(3)
Freundlich (Linearized)	$\log \dfrac{X}{m} = \log k_f + \dfrac{1}{n}\log C_e$	$\log \dfrac{X}{m} = \log p + q\log C_e$ $p=k_f,\ q=1/n$	...(4)
Modified Langmuir Type 1 (Mlang1)	$\dfrac{X}{m} = \dfrac{bV_m C_D^{\,c}}{1+bC_e}$	$\dfrac{X}{m} = \dfrac{pq\,C_D^{\,y}}{1+p\,C_e^{\,s}}$ $p=b,\ q=V_m,\ r=c$	...(5)
Modified Langmuir Type 2 (Mlang2)	$\dfrac{X}{m} = \dfrac{bV_m C_D^{\,y}}{1+bC_e^{\,d}}$	$\dfrac{X}{m} = \dfrac{pq\,C_D^{\,y}}{1+p\,C_e^{\,s}}$ $p=b,\ q=V_m,\ r=c,\ s=d$	...(6)
Modified Freundlich (Mfreund)	$\dfrac{X}{m} = k_f C_0^{\,1/n}$	$\dfrac{X}{m} = p\,C_D^{\,r}\,C_e^{\,q}$ $p=k_f,\ q=1/n,\ r=a$	...(7)

b = Langmuir parameter (adsorption bond energy), V_m = Langmuir parameter (monolayer coverage),
C_e = adsorbate concentration at adsorption equilibrium,
$\dfrac{X}{m}$ = adsorbate adsorbed per unit weight of the adsorbent

Langmuir isotherm, initially developed for describing adsorption of gases on solid surface, assumes equal energy status for all adsorption sites, one adsorbate specie per adsorption site (monolayer coverage) and no mutual interaction between adsorbed adsorbate species.

Freundlich isotherm, on the other hand, is an empirical relationship which considers adsorption sites may be of varying energy and hence multi layer adsorption is a possibility. It may be observed that in both Langmuir and Freundlich isotherms only equilibrium concentration is considered and initial concentration does not find any space. In fact this is true not only for Langmuir and Freundlich isotherms but for other isotherms as well. It was felt that initial concentration, C_0 was a more fundamental variant as adsorption varied non linearly with initial concentration. Based on this argument modified Langmuir and Freundlich isotherms have been proposed in this work where initial concentration C_0 has been incorporated in the conventional Langmuir and Freundlich forms and all experimental adsorption data have been modeled with conventional as well as modified isotherms. Proposed modified Langmuir and Freundlich isotherms have also been shown in Table 1.

Column 3 in Table 1 expresses various isotherm parameters in terms of p, q, r and s. The correspondence between p, q, r, s and pertinent isotherm parameters has also been shown in column 3 of Table 1 side by side. This was done for the ease of reporting different isotherm parameters in terms of p, q, r and s.

Both Langmuir and Freundlich forms (Eqn. 1 and 2 in Table 1) may be linearized as may be seen also in Table 1 (Eqn. 3 and 4). If the experimental adsorption data follow Langmuir isotherm then plot of $\frac{1}{(X/m)}$ with $\frac{1}{C_e}$ should be a straight line and parameters V_m and b may be calculated from the intercept and slope respectively. Similarly if the data follow Freundlich model, plot of $\log \frac{X}{m}$ with $\log C_e$ should yield a straight line and parameters kf and n may be calculated from the intercept and slope respectively. Alternatively Langmuir and Freundlich parameters may also be obtained through direct and robust optimization of Eqn. 1 and 2 using some appropriate optimization algorithm. In the present work SOLVER optimization programme available in MS-Excel was used for this purpose.

Table 2 shows employability of various isotherm models shown in Table 1 in respect of Pb(II) and Cd(II) adsorption data on $Fe^{II}SPT$ and $Fe^{III}SPT$. Column 1 in Table 2 shows adsorbate-adsorbent pair and column 2 the employed isotherm model. Columns 3-6 list various isotherm parameters in terms of p, q, r and s. Correspondence of p, q, r and s with the respective isotherm parameters may be obtained in Column 3 of Table 1. Column 6 shows the optimized Sum Square Error (SSE) for each model. SSE has been defined as.

$$SSE = \sum_{i=1}^{n} [(\frac{X}{m})_i \exp. - (\frac{X}{m})_i cal.]^2 \qquad \ldots (8)$$

Where $(\frac{X}{m})_i$ exp. and $(\frac{X}{m})_i$ cal. are respectively the experimental and predicted adsorption data for each adsorption experiments using optimized model parameters for prediction.

SSE was minimized during robust optimization for obtaining isotherm parameters using SOLVER programme. In case of linearized models, however, SSE was calculated using isotherm parameters obtained from the slope and intercept of the regressed straight line. Column 7 shows goodness of the fit between $(\frac{X}{m})_i$ exp. and $(\frac{X}{m})_i$ cal.

By the first look at Table 2, one may easily find that robust optimization through SOLVER technique consistently returns better SSE and R^2 values as compared to linearized models in both Langmuir and Freundlich types. This automatically implies that parameters obtained

Table 2 : Employability of various isotherm models shown in Table 1 with reference to the experimental Pb(II) and Cd(II) adsorption data on $Fe^{II}SPT$ and $Fe^{III}SPT$

		p	q	r	s	SSE	R2
Pb- FeIISPT	Langmuir (Linearized)	0.094	190.67			5469	0.799
	Langmuir	0.03	252.39			1999	0.918
	Mlang1	0.05	29.20	1.34		338	0.982
	Mlang2	0.00	1.21E+05	0.55	1.42	195	0.989
	Freundlich (Linearized)	43.03	0.30			689	0.96
	Freundlich	26.93	0.37			823	0.94
	Mfreund	0.98	0.94	0.83		76915	0.997
Pb- FeIIISPT	Langmuir (Linearized)	1.86	277.8			17408	0.66
	Langmuir	0.28	335.84			11456	0.846
	Mlang1	0.03	46.01	1.33		389	0.993
	Mlang2	0.03	219.02	0.93	0.83	22	0.999
	Freundlich (Linearized)	135.97	0.18			116	0.997
	Freundlich	50.23	0.35			2798	0.876
	Mfreund	150.19	0.19	0.03		95	0.805
Cd- FeIISPT	Langmuir (Linearized)	0.054	106.11			564	0.87
	Langmuir	0.03	121.20			342	0.911
	Mlang1	0.08	21.26	1.28		76	0.978
	Mlang2	0.09	23.02	1.22	0.95	76	0.978
	Freundlich (Linearized)	22.77	0.28			120	0.967
	Freundlich	19.07	0.31			127	0.964
	Mfreund	27.62	0.45	0.20		114	0.968
Cd- FeIIISPT	Langmuir (Linearized)	0.082	227.05			806	0.94
	Langmuir	0.10	218.85			680	0.946
	Mlang1	0.04	62.56	1.20		3	0.999
	Mlang2	0.04	56.39	1.25	1.03	0	1
	Freundlich (Linearized)	62.22	0.23			1782	0.87
	Freundlich	47.22	0.27			1558	0.878
	Mfreund	90.19	0.28	0.12		1416	0.889

Literature data on some adsorbents with high Pb(II) and Cd(II) loading capacity have been listed in Table 3 along with the ones obtained from the present study for $Fe^{II}SPT$ and $Fe^{III}SPT$ for the purpose of comparison. Loading capacities reported for $Fe^{II}SPT$ and $Fe^{III}SPT$ in Table 3 are essentially parameter V_m, in Langmuir isotherm obtained through SOLVER optimization. It was interesting to note that Pb(II) and Cd(II) loading capacities of $Fe^{II}SPT$ and $Fe^{III}SPT$ were much higher than others in Table 3. While this observation is heartening, these numbers should be judged with due caution.

It must be borne in mind that the loading capacity reported for $Fe^{II}SPT$ and $Fe^{III}SPT$ in Table 3 may not be the true loading capacity as these have been obtained at a single adsorbent weight.

through SOLVER are more realistic and trustworthy than those obtained through linearization. SSE value obtained from linearization, in all likelihood, represents local minimum on the error surface while through SOLVER optimization it is possible to reach the global minimum. However, it has also been observed that proper initial parameter guess is critical in reaching the global minimum. This is especially true when error surface comprises several minima of comparable depth. SOLVER optimization also returns absurd parameters when the error surface is flat around the minimum and SSE becomes relatively insensitive to the change of parameters.

One may observe that in the case of $Fe^{II}SPT$ the parameter 'p' in the Langmuir model which corresponds to adsorption bond energy parameter 'b' in the parent equation is small and consistently smaller than the corresponding 'p' values in $Fe^{III}SPT$. This implies that Pb(II) and Cd(II) are not only weakly held by $Fe^{II}SPT$ but between the two $Fe^{II}SPT$ is a weaker adsorbent than $Fe^{III}SPT$ in respect of Pb(II) and Cd(II).

It may be observed in Table 2 that Pb- $Fe^{II}SPT$, Pb- $Fe^{III}SPT$ and Cd-$Fe^{III}SPT$ pairs fit better into Freundlich model whereas Cd-$Fe^{III}SPT$ pair conforms to Langmuir model better. Keeping in view various assumptions in both Langmuir and Freundlich isotherms models and their forced employment into adsorption of ions on solid surface in aqueous medium, match or mismatch to any model must be dealt with utmost caution. It is not practically possible to ensure equal energy status of all adsorption sites or monolayer coverage on the adsorbent surface as presumed in the Langmuir model. To address this column various models have been proposed by amalgamating Langmuir and Freundlich types in one isotherm. Though these isotherms have not been considered in the present study, the point remains pertinent that no adsorption can be and should be identified as solely monolayer or multilayer.

Table 2 also lists performance of newly proposed modified isotherms, namely, Mlang1 (Modified Langmuir-Type1), Mlang2 (Modified Langmuir-Type2), Mfreund (Modified Freundlich). In all of them initial concentration C0 has been introduced along with C_e as may be seen in Table 1. In Mlang1 eqn. 1 has been modified by replacing C_e in the numerator with C_0^c. In Mlang2 eqn. 1 has been modified by replacing Ce in the numerator with C_0^c and C_e in the denominator with C_e^d. Exponents c and d are newly introduced parameters in the proposed modified Langmuir forms. Similarly in Mfreund, eqn. 2 has been modified by introducing a new factor C_0^b where b is a newly introduced parameter.

It was observed with gratification that newly proposed models remarkably improved the quality of the isotherms. Especially Mlang1 showed significant improvement over conventional Langmuir form while Mlang2 improved it further. Mfreund also showed improvement over conventional Freundlich model. Between the two Modified Langmuirs performed better than modified Freundlich.

It is important to mention at this stage that even though modified isotherms improve the fit, physical significance of isotherm parameters somewhat remain obscure. For example, b and V_m in conventional Langmuir form represent adsorption bond energy and monolayer coverage (loading capacity) respectively. However, in Mlang1 and Mlang2 they need not necessarily mean the same. Similarly k_f and n in conventional Freundlich form need not necessarily represent the same quantities in Mfreund.

Table 3 : Comparison of Pb(II) and Cd(II) loading capacity of Fe^{II}SPT and Fe^{III}SPT with some high loading adsorbents.

Adsorbent	Loading capacity mg g^{-1}		References
	Pb(II)	Cd(II)	
Red mud		13.0	[13]
Rice husk	11.0		[14]
Chromite mine overburden	27.54	22.4	[15]
Nickel laterite (low iron)	28.4	11.0	[16]
Nickel laterite (high iron)	44.4	13.2	[16]
Red bauxite	64.3	38.7	[17]
Iron ore slime	63.5	34.7	[18]
Water washed clay		11.6	[19]
Chemically treated clay	48.1	12.6	[19]
Washed and treated clay	52.6	24.4	[19]
Low grade manganese ore	142.8	59.1	[20]
Meranti sawdust	34.2		[21]
Clinoptilolite	124		[20]
Blast furnace sludge	64.2		[22]
Fe^{II}SPT	252.3	121.2	Present work
Fe^{III}SPT	335.8	218.8	Present work

Normally loading capacity is a function of both adsorbent weight and initial adsorbate concentration and true loading capacity should be an optimal combination of both. Further,

$$\frac{1}{1 + bC_e}$$

Table 4 : R_L values obtained for Pb(II) and Cd(II) adsorption on $Fe^{II}SPT$ and $Fe^{III}SPT$ using 'b' values estimated with SOLVER

Metal ion	Initial concn., C_0, mg l^{-1}	$Fe^{II}SPT$		$Fe^{III}SPT$	
		Final concn., C_e, mg l^{-1}	R_L	Final concn., C_e, mg l^{-1}	R_L
Pb(II)	22.9	6.94	0.82	0.36	0.91
	42.4	21.82	0.59	5.32	0.40
	94.3	65.51	0.32	41.85	0.08
	171.6	129.86	0.19	106.94	0.03
	408.6	360	0.08	332.56	0.01
Cd(II)	22.3	13.18	0.70	6.68	0.60
	44.4	31.62	0.49	15.29	0.40
	95.2	80.55	0.27	60.2	0.15
	186.3	164.52	0.16	146.2	0.07
	427.9	404.04	0.07	382.64	0.03

parameters were obtained through linearization of the isotherms as well as through direct and robust optimization of the parent isotherm equations. Robust optimization always led to much superior fit in terms of sum square error (SSE) and goodness of the fit between experimental and calculated adsorption data using optimized isotherm parameters. Freundlich model performed better for Pb(II) adsorption data over both $Fe^{II}SPT$ and $Fe^{III}SPT$ and Cd(II) adsorption over $Fe^{II}SPT$. However, it was Langmuir model that performed better for Cd(II) adsorption over $Fe^{III}SPT$. Keeping in view the inherent assumptions/inadequacies in the Langmuir and Freundlich isotherm fit to any model should be judged with caution as in practice no adsorption can be described as fully Freundlich or Langmuir type. Loading capacity of $Fe^{III}SPT$ and $Fe^{II}SPT$ which is the monolayer coverage Vm in Langmuir isotherm, obtained through robust optimization was respectively 218.8 and 121.2 mg g^{-1} for Cd(II) and 335.8 and 252.4 mg g-1 for Pb(II). While these figures indicate superior nature of $Fe^{II}SPT$ and $Fe^{III}SPT$ as Pb(II) and Cd(II) adsorbents over many, these figures must be handled with caution as there is chance of inflation. As a test, loading capacity obtained from the isotherms should match with those obtained from non isotherm approach. Newly proposed modified Langmuir and Freundlich isotherms, in which initial concentration was introduced, were very impressive in terms of SSE and goodness of the fit. However, the physical significance of the parameters therein must be ascertained. All adsorptions were found to be favourable over the studied initial concentration range which moved towards irreversibility as the initial concentration was increased.

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