Electronic Supplementary Information (ESI)

Organic Free Low Temperature Direct Synthesis of Hierarchical Protonated Layered Titanates/ Anatase TiO$_2$ hollow spheres and Their Task-Specific Applications

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Detailed synthetic procedure:

Materials. Titanium isopropoxide was purchased from Sigma Aldrich, USA. Ethanol, ammonium hydroxide, ammonium carbonate, lead nitrate, methylene blue were purchased from S. D. Fine-Chem. Limited, India. All the chemicals were used without further

purification. For all applications water with a resistivity of 18 MΩ cm was used, obtained from a Millipore water purifier.

Preparation of titanium peroxo carbonate precursor solution: The titanium peroxo carbonate precursor solution was prepared following the procedure as reported earlier.[1] In a typical procedure, the titanium hydroxide was precipitated from 0.01 mole titanium iso-propoxide using a solution containing water, methanol and ammonia solution. After filtration and washing, to the resultant muddy titanium hydroxide, 25 ml of 1.6 molar aqueous ammonium carbonate solution was added under constant stirring followed by addition of 3 ml 30% H_2O_2 which resulted in a light yellow colored clear precursor solution. The volume of the solution was made 30 ml by adding de-ionized water.

Synthesis of hierarchical spheres of protonated layered titanates: The hierarchical spheres of protonated layered titanates were synthesized by hydrothermal method. In a typical procedure, to the above prepared 30 ml titanium peroxo carbonate precursor solution 50 ml ammonium hydroxide solution (30%) and 20 ml de-ionized water was added to make a 100 ml solution. Then, from the resultant 100 ml solution, containing titanium peroxo carbonate precursor and ammonium hydroxide, 33 ml was transferred to 50 ml Teflon lined stainless steel autoclave, sealed properly and transferred to a pre-heated electrical oven. After hydrothermal treatment at 110 °C for 24h, the resultant precipitate was filtered, washed with de-ionized water followed by ethanol and dried overnight at ambient conditions. Materials were also synthesized using varying amount of ammonium hydroxide solution (30%) [60/ 40/ 30/ 20/10/0 ml] instead of 50 ml, keeping total volume of the solution mixture 100 ml supplementing with de-ionized water. The synthesized products were named as HPLTHS-x, where "x" is amount of ammonium hydroxide solution used. Such as, HPLTHS-50 stands for the sample synthesized using 50 ml of ammonium carbonate.

Synthesis of hierarchical spheres of TiO$_2$: For the synthesis of corresponding TiO$_2$, the as-synthesized products were calcined in air at 400°C for 2h in a heating rate of 1°C/min.

Characterizations: Powder X-ray diffraction patterns were recorded in the 2θ range of 20-80° on a Philips X'pert X-ray powder diffractometer using Cu Kα (λ= 1.54178 Å) radiation. Thermo gravimetric analysis (TGA) was performed on Mettler-Toledo (TGA/SDTA 851^e) in air at a heating rate of 10 °C/min. The nitrogen adsorption - desorption measurements at 77 K were performed on ASAP 2010 Micromeritics, USA, after degassing samples under vacuum (10^{-2} torr) at 250 °C for 4 h. The surface area was determined by Brunauer-Emmett-Teller (BET) equation. Pore size distributions were determined using BJH model of cylindrical pore approximation. A scanning electron microscope (SEM) (Leo series 1430 VP) equipped with INCA was used to determine the morphology of samples. The sample powder was supported on aluminum stubs and then coated with gold by plasma prior to measurement. Transmission electronic microscope (TEM) images were collected using a JEOL JEM 2100 microscope and samples were prepared by mounting an ethanol dispersed samples on lacey carbon formvar coated Cu grid.

Preparation of sectioned spheres (through microtomy): As-synthesised sample HPLTS-50 was embedded in spur resin and polymerised by heating at 80 degree celcius for 12 hours in air oven. Sections were cut, on LEICA EM UC6, of around 300nm thickness using a glass knife. These sections were collected on a carbon coated Cu grid and analysed under TEM microscope.

Adsorption experiment: The Pb^{2+} and Methylene blue (MB) dye sorption experiments were carried out using aqueous solution of Pb(NO$_3$)$_2$ and MB at 30°C in a 150 ml conical flask in a shaking water bath (Julabo- SW23) at 130 rpm.

Pb^{2+} sorption isotherm was obtained by equilibrating 50 mg of HPLTHS-50 in 50 ml of aqueous Pb(NO$_3$)$_2$ solution of different concentrations (100-600 ppm) at pH ~ 5 for 24h. Adsorbent was separated after equilibrium by centrifugation. Concentration of Pb^{2+} before and after adsorption was estimated by EDTA titration, using xylenol orange as an indicator and hexamine as buffer (pH ~ 5.0) [2, 3]. Amount of Pb^{2+} adsorbed on the HPLTHS was calculated using equation 1.

$$Q_e = \frac{(C_0 - C_e)V}{m}$$

(1)

Where, Q_e = amount of Pb^{2+} adsorbed on adsorbent at equilibrium (mg g^{-1}), C_0 = initial concentration of Pb^{2+} solution (mg L^{-1}), C_e = concentration of Pb^{2+} in solution at equilibrium (mg L^{-1}), m = mass of adsorbent used (g) and V = volume of Pb solution (L).

In order to investigate the adsorption rate, 50 mg of HPLTHS-50 was suspended in 50 ml of 600 ppm aqueous Pb^{2+} solution and equilibrated for different time intervals from 0 to 24 h at 30 °C while shaking on the water bath at 130 rpm. Quantity of adsorbate adsorbed at time t was calculated using equation 1.

MB sorption isotherm was obtained by equilibrating 50 mg of HPLTHS-50 with 100 ppm aqueous solution of MB for 24h with different volume range of 50 to 200 ml at pH ~ 9.5-10, while shaking on shaking water bath (Julabo- SW23) at 130 rpm. Concentration of MB was analyzed spectrophotometrically at 664 nm (UV 2550 spectrophotometer, Shimadzu) before and after adsorption for adsorption isotherm and kinetic studies. Quantity of adsorbate adsorbed was calculated using equation 1.

Where, Q_e = amount of MB adsorbed on adsorbent at equilibrium (mg g^{-1}), C_0 = initial concentration of MB solution (mg L^{-1}), C_e = concentration of MB in solution at equilibrium (mg L^{-1}), m = mass of adsorbent used (g) and V = volume of MB solution (L).

In order to investigate the adsorption rate of MB, 50 mg of HPLTHS-50 was suspended in 100 ml of 100 ppm aqueous MB blue solution and equilibrated for different time intervals

from 0 to 24 h at 30 °C while shaking on shaking water bath (Julabo- SW23) at 130 rpm. Quantity of adsorbate adsorbed at time t was calculated using equation 1.

Photocatalytic degradation of methylene blue: Photocatalytic efficiency of the synthesized spherical TiO_2 obtained by calcination of the HPLTHS-50 was evaluated by degradation of MB^+. In a typical reaction 0.025 g TiO_2 catalyst was suspended in 180 ml of MB^+ solution of concentration 20 mgL^{-1}. A previously reported photocatalytic reactor was used for all the photocatalytic studies.[4] Prior to UV irradiation with 125W mercury vapour lamp (Crompton, high-pressure mercury vapour lamp, with the glass bulb removed), the dispersion in the reactor was magnetically stirred in the dark for 30 minutes and was irradiated with UV light for 90 minutes. During Photocatalytic reaction, samples (3 ml) were withdrawn by syringe from the irradiated suspension in a regular interval (0, 10, 30, 45, 60, 75 and 90 minutes). Collected samples were centrifuged at 15000 rpm to separate the catalyst and concentration of MB was determined by a UV-visible spectrophotometer (Shimadzu-160A). The reaction was repeated for 4 times. Each time the same catalyst was recovered by centrifuge and used to check the reusability.

Electrochemical measurement: TiO_2 electrodes for electrochemical lithium insertion studies were prepared by blade-coating a slurry of 70 wt.% of the TiO_2, 20 wt.% of poly(vinylidene fluoride) and 10 wt.% MCMB dispersed in *N*-methyl-2-pyrrolydone on a copper foil, followed by drying at 110 °C in an air oven, roller-pressing the dried sheets, and punching out circular sheets. The TiO_2 electrodes were coupled with lithium (Foote Minerals) and an electrolyte of 1M $LiPF_6$ in a 1:1 (v/v) mixture of EC-DEC in swage-lock cells in an argon-filled glove box (M Braun, Germany). Galvanostatic charge–discharge profiles were made between 2.500 and 0.020V on a computer-controlled battery testing unit (Maccor, 4000, USA).
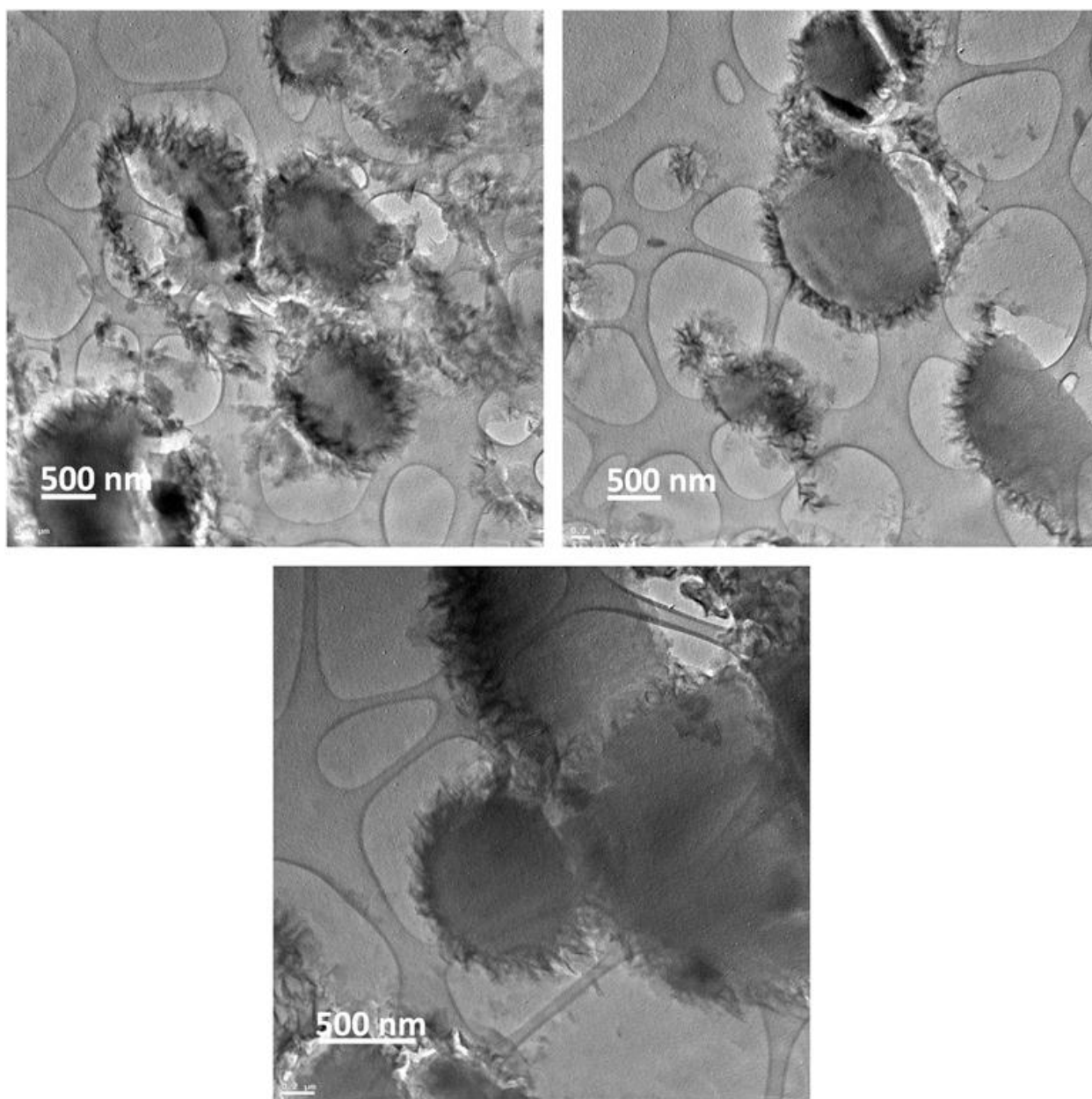
Fig. S1.   TEM images of the sectioned spheres through microtomy.

Table S1: t-Plot Report of HPLTS-50 and anatase TiO_2.

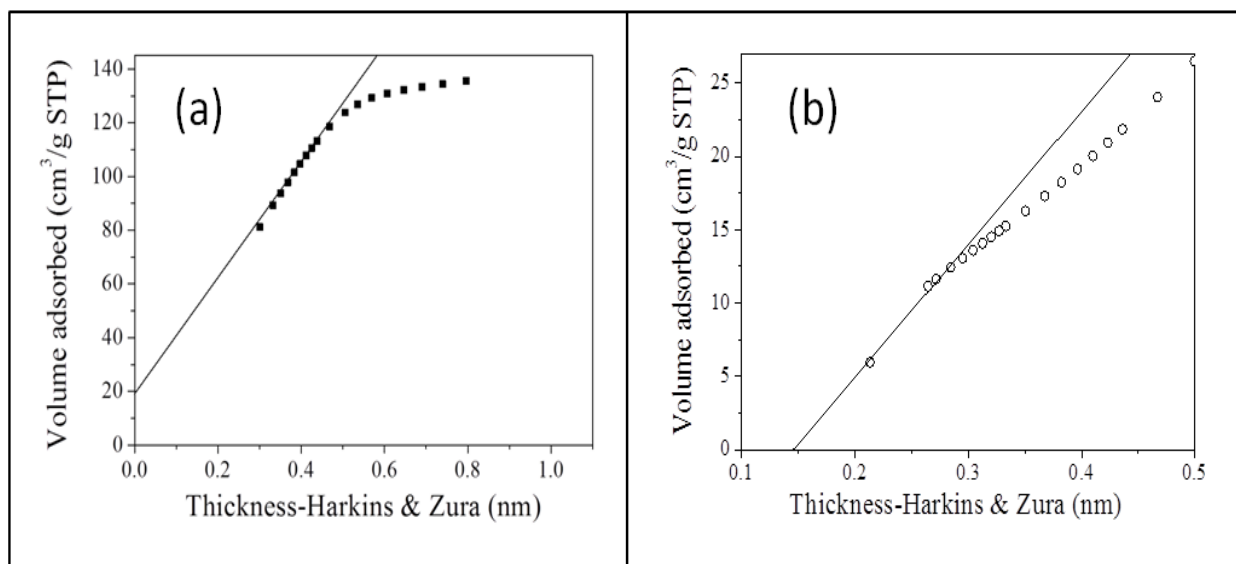| Sample	Micropore Volume (cm³/g)	Micropore Area (m²/g)
HPLTS	0.031	76.783
Anatase TiO_2	0	0

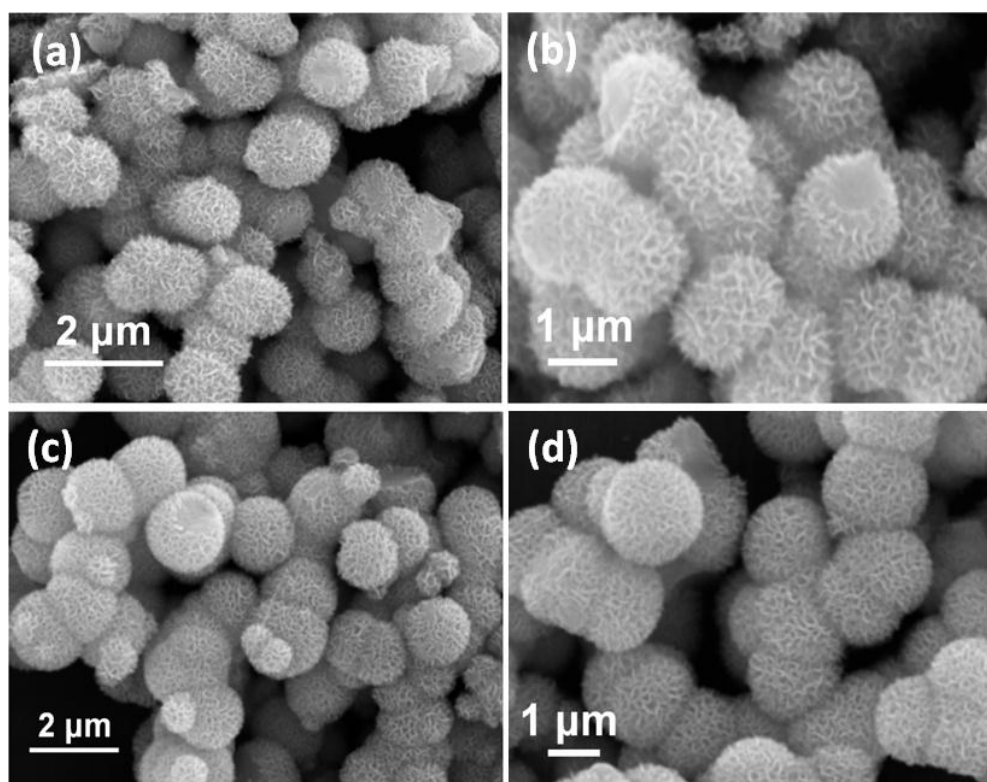**Fig.S2:** t-plot of (a) HPLTS-50 and (b) anatase TiO_2.

Fig.S3. (a) & (b) SEM images of HPLTS prepared with 70ml NH_3 solution (HPLTS-70), (c) & (d) SEM images of (HPLTS-60) prepared with 60ml NH_3 solution.
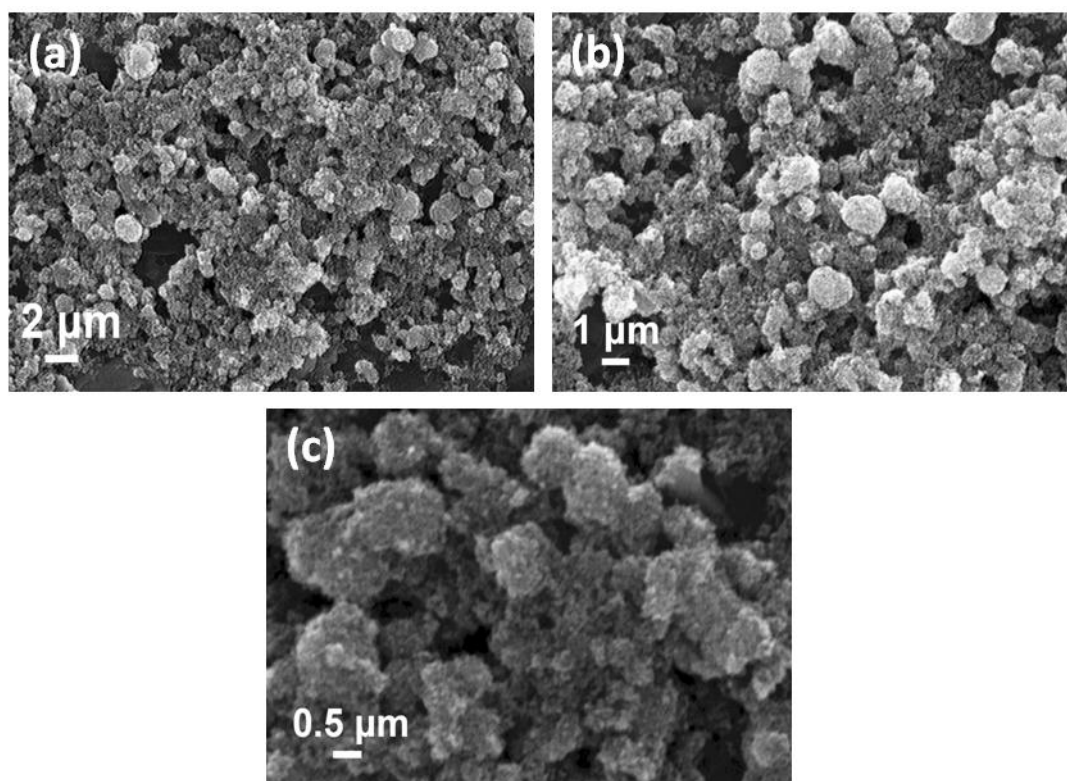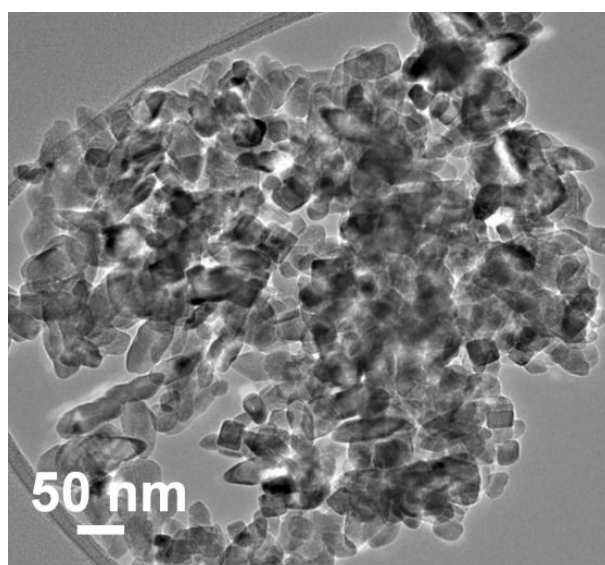
Fig.S4. (a), (b) & (c) SEM images of HPLTS prepared at 130°C.

FigS5. (a) & (b) TEM images of HPLTS prepared at 130°C.

Adsorption Kinetics:

Kinetic nature of the ion exchange property of synthesized layered titanate was verified for pseudosecond-order kinetic models.[5] The pseudo-second-order expression is given as

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$$

(1)

Where, q_e is the amount adsorbed (mg g^{-1}) at equilibrium, and q_t is the amount adsorbed after time t (h). K is the rate constant for pseudo-second-order adsorption (g mg^{-1}min^{-1}). Values of K are estimated from the intercept of t/q versus t plots using equation 1. Feasibility of the kinetic path was examined from the values of rate constants (K) and correlation coefficient (R^2) (Table S2 and S3) respectively. Good agreement of the R^2 close to unity indicated that the sorption of Pb^{2+} and MB^+ on the HPLTS obeys pseudo- second order kinetics.

Table S2. Values of the correlation coefficient R^2, q_e and equilibrium constant K parameters calculated for kinetic studies of Pb^{2+} and MB^+ on HPLTS-50.

Adsorbate	R^2	q_e experimental (mg g^{-1})	q_e calculated (mg g^{-1})	K (g mg^{-1}min^{-1})
Pb^{2+}	0.9999	335	333	4.5×10^{-2}
MB^+	0.9993	153	158	3.9×10^{-2}

Table S3. Equilibrium model equations; slope and intercept for the isotherm equations [a].

Non Linear Form	Linear form	Slope	Intercept
	Langmuir isotherm[6-10]		
$Q_e = \dfrac{Q_m K_L C_e}{1 + K_L C_e}$	$\dfrac{C_e}{Q_e} = \dfrac{1}{Q_m} C_e + \dfrac{1}{K_L Q_m}$	$\dfrac{1}{Q_m}$	$\dfrac{1}{K_L Q_m}$
	Sips isotherm[11,12]		
$Q_e = \dfrac{Q_m K_S C_e^{1/n}}{1 + K_S C_e^{1/n}}$	$\dfrac{C_e^{1/n}}{Q_e} = \dfrac{1}{Q_m} C_e^{1/n} + \dfrac{1}{K_S Q_m}$	$\dfrac{1}{Q_m}$	$\dfrac{1}{K_S Q_m}$
	Redlich–Peterson[13,14]		
$Q_e = \dfrac{K_{RP} C_e}{1 + \alpha C_e^{\beta}}$	$ln\left[K_{RP} \dfrac{C_e}{Q_e} - 1 \right] = \beta ln(C_e) + ln(\alpha)$	β	$ln(\alpha)$

[a] C_e = dye concentration at equilibrium (mg L^{-1}); Qe = equilibrium adsorption capacity (mg g^{-1}); K_L = Langmuir adsorption constant (L mg^{-1}); Qm = maximum adsorption capacity (mg g^{-1}); K_S = Sips constant (L g^{-1}); n = heterogeneity factor. K_{RP} = constant that is varied to maximize the linear correlation coefficient (r^2), (L g^{-1}); α = constant (mg L^{-1})$^{-\beta}$; β = Redlich–Peterson exponent (dimensionless).

Langmuir isotherm was obtained by ploting C_e/q_e versus C_e, SIPS isotherm was obtained by

ploting $C_e{}^n/q_e$ against $C_e{}^n$ and Redlich–Peterson isotherm was obtained by ploting against

$ln(KrC_e/Q_e - 1)$ against $ln\ C_e$ (Figure S5-S6). Linier fit of these respective isotherms gave the

value of R^2. These values of R^2 along with saturation capacity (Qm), equilibrium constants of

Langmuir (K_L), SIPS (Ks) and Redlich-Peterson (K_{RP}) where calculated using the slope and
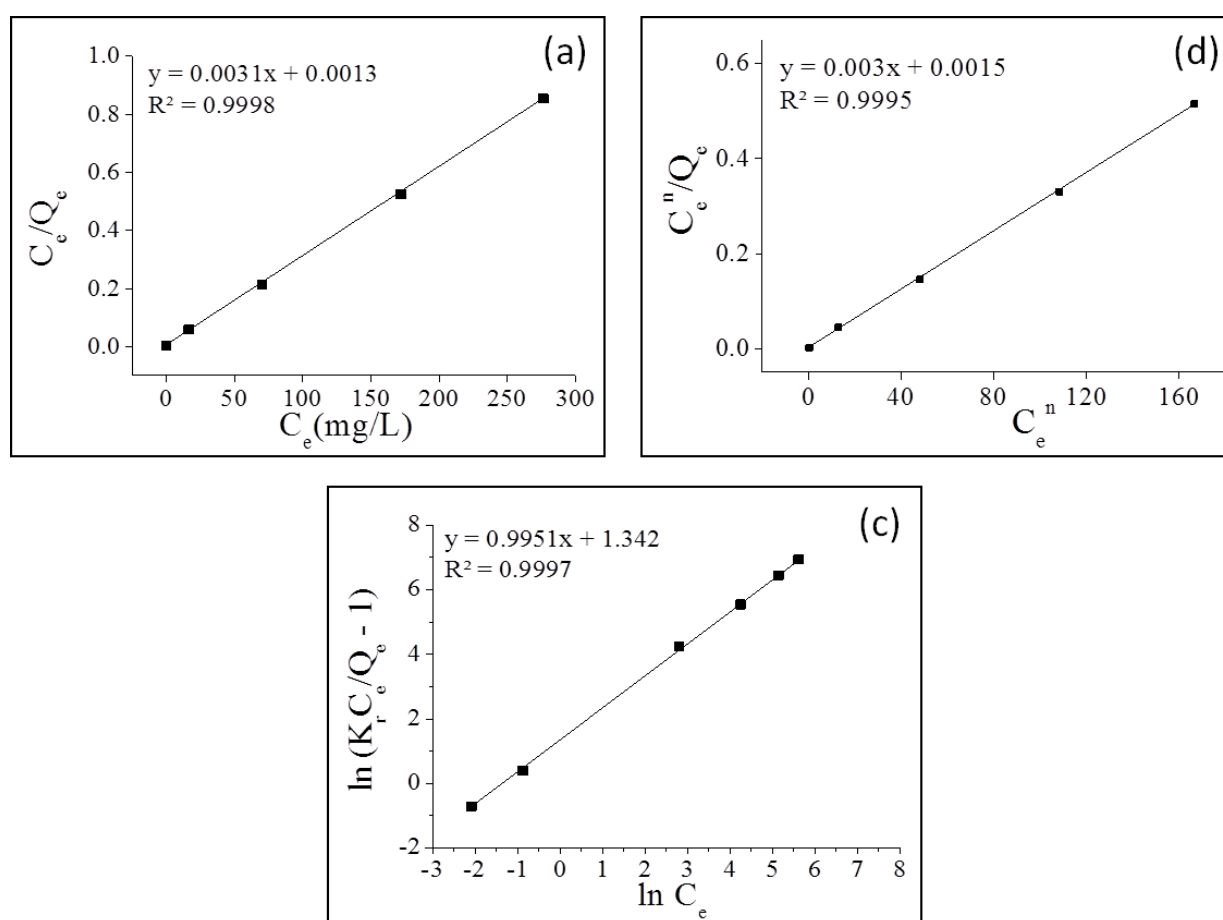
intercept obtained for the respective models (Table 2).

Fig. S6. Linear fitting of different isotherm models (a) Langmuir, (b) SIPS, (c) Redlich–Peterson for adsorption of Pb^{2+}.
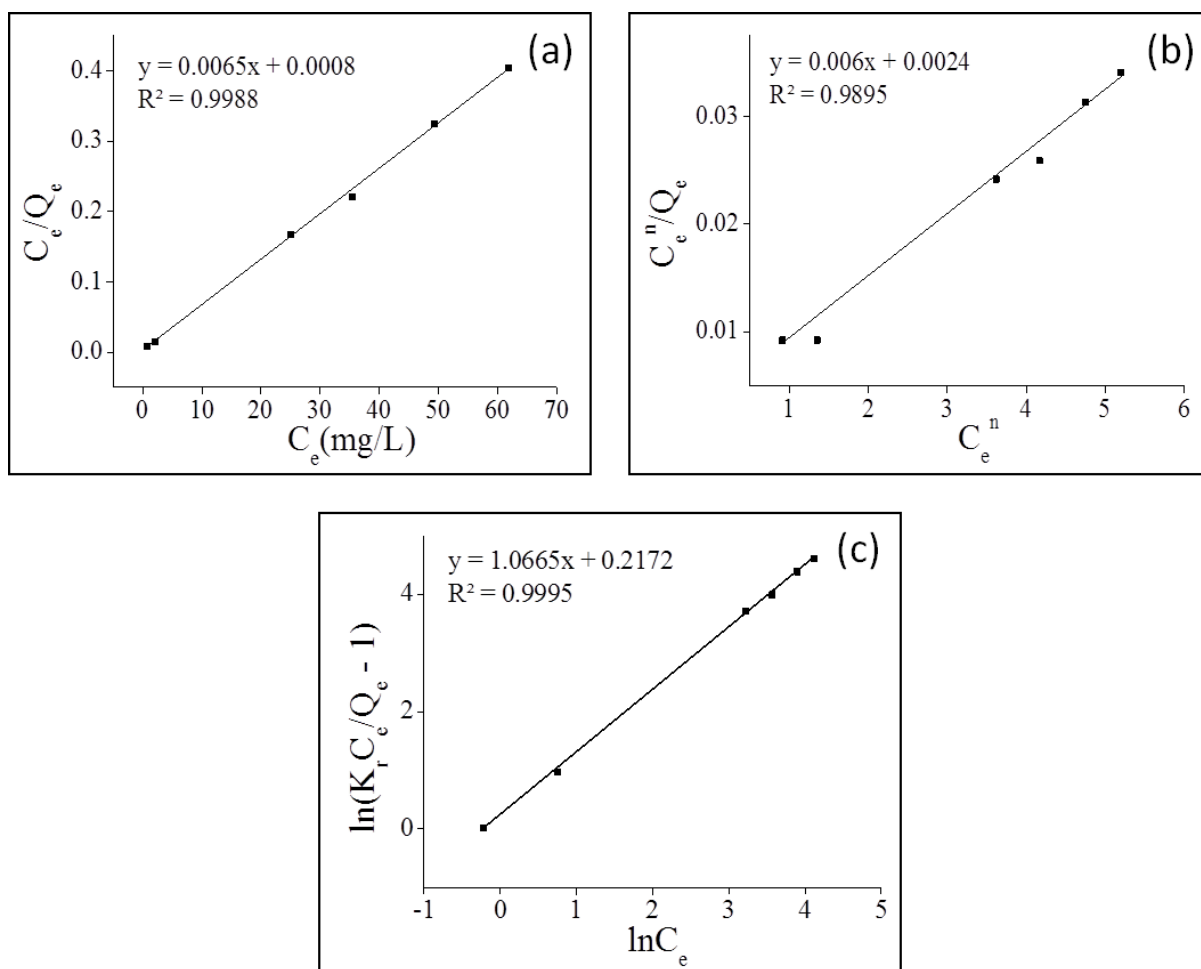
Fig. S7. Linear fitting of different isotherm models (a) Langmuir, (b) SIPS, (c) Redlich–Peterson for adsorption of MB^+ on HPLTS.

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