A cationic porous polymer as robust and recyclable adsorbent for the removal of anionic dyes from aqueous contaminants

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Supplementary Information

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Section S1:

Chemicals Used:

The chemical used in this work are mentioned below with corresponding manufacturers are also mentioned by parenthesis and their using protocol when necessary.

a) Triallylamine (Sigma-Aldrich, India).

b) (p-Vinylbenzyl)trimethylammonium chloride (Sigma-Aldrich, India).

c) N,N,N",N"-tetramethylethylenediamine (Spectrochem, India).

d) Ammonium persulfate(Lobachem, India).

e) Sodium Hydroxide and Sodium Chloride (Lobachem, India).

f) Rose Bengal disodium salt (Lobachem, India) and Xylenol orange tetrasodium salt (Spectrochem, India) and these substrates were used for the application studies.

g) Hydrochloric acid, Methanol and all other solvents used were of analytical grade (Merck, India).

Here all chemicals were used without further purification and all solvents were distilled prior to use.

Section S2:

Characterization Technique and Instrumentation:

Filtration by centrifugation was done by using R8C Remi bench Centrifuge at 4500 operating rpm. Ultrasound Treatment was applied by using Digital Ultrasound Cleaner Instrument; Model No. LMUC-3 at an applied operating power of 100W with frequency 40KHz. The entire pH variation studies were carried out using OAKTON-700 Digital Electrode pH meter at room temperature. Before using every time the instrument was calibrated using company supplied buffer solution of different pH. Zita potential was measured by using Malvern Zeta Potential Instrument; Model No. ZEN-3600. The entire FT-IR spectrum was recorded on transmittance mode by using Perkin-Elmer, Spectrum 100 FTIR Spectrometer. ^{1}H NMR spectrum of the monomer was recorded on Bruker Advance 500 MHz NMR spectrometer. Solid-state 13C CP-MAS NMR study was performed using Bruker Advanced-II 600 MHz MAS-NMR spectrometer with a MAS frequency of 8 kHz by using a 4nm MAS probe. Powder X-ray diffraction studies were carried out with Bruker D8 Advance X-ray diffractometer using Ni-filtered Cu Kα (λ = 0.15406 nm) radiation as X-ray source. Thermogravimetric Analysis (TGA) measurement was carried out using Perkin Elmer TA-SDT Q-600 thermal analyzer under compressed air flow with heating rate 10°C/min. N_2 adsorption/desorption studies were performed with an Quantachrome Instruments, i-Sorb-HP1 surface analyzer (Quantachrome Instruments, USA) at 77 K. Prior to the measurement, the sample was degassed in vacuum at 150°C for 6h to remove all the guest molecules present within the material. The specific surface area was estimated by using BET model and the PSD of the VBT-POP was derived by the NLDFT method from adsorption branch of the isotherm. Entire external morphological studies of the VBT-POP along with all associated studies EDS analysis and Elemental mapping were done in JEOL JEM 6700 FE-SEM instrument with EDS attachment, operated at 1 – 20 kV. The entire series of UV-Vis analysis were executed by using Agilent Cary Series UV-Vis –NIR spctrophotometer model No. Cary -5000 UV-Vis NIR.

Section S3:

General procedure for dye adsorption studies by employing VBT-POP:

POPs containing aliphatic nitrogen network along with cationic centers are unique adsorbent platform for the removal of anionic dyes from their aqueous solution. Here also keeping in mind of that property the aqueous solutions of two anionic dyes Rose Bengal disodium salt (abbreviated as RB) and Xylenol Orange tetrasodium salt (abbreviated as XO) were separately employed for the dye adsorption studies. In a typical adsorption experiment 500 PPM 10 mL solutions of each of RB and XO was taken in an oven dried clean loosely caped glass vial and to that 8 mg and 16 mg VBT-POP (without further activation via hot oven) material was added respectively with continuous stirring at 1200 rpm for 30 minutes at room temperature under air. 2 ml supernatant aliquots were collected from both the dye solutions after stopping the mechanical agitation. Both the aliquots were further centrifuged for 2-3 minutes at 4500 rpm so as to remove if any residual material from the supernatant. Finally 1 mL adsorbent free supernatant was collected from the centrifuged aqueous part and the individual residual concentration of dye was determined and compared to their respective raw solution using UV-vis spectroscopy (at λmax_{RB} = 545 nm and λmax_{XO} = 433 nm).

Section S4:

Optimization of Adsorbent Dosage:

Dose optimization of the VBT-POP material for the adsorptive removal of RB and XO dyes from their aqueous solution was performed by batch adsorption experiments. In every 10 ml of 500 ppm RB and XO solution of batch of each, 2, 4, 6, 8, 10 mg; and 8, 10, 12, 14, 16, mg VBT-POP was added respectively and stirred at 1200 rpm for 30 min at room temperature in a loosely caped glass vial under air. Then the solution was centrifuged to filter up the adsorbent and the final adsorbent free clear supernatant was collected and analyzed through UV-Vis spectroscopy (at $\lambda max_{RB} = 545$ nm and $\lambda max_{XO} = 433$ nm). And compared their respective absorbance maxima with the raw dye solution so as to determine the respective residual dye concentrations.

Section S5:

Optimization of Adsorbent Treatment Time along with Adsorption Kinetics Studies:

Here in a typical experiment 40 ml of 500 ppm RB and XO solutions have been treated with 30 mg and 60 mg of VBT-POP respectively and the solutions was stirred at 1200 rpm at room temperature in a loosely caped glass vial under air. After specific time intervals, 2 ml aliquots from the respective mixture were taken very quickly from the system; filtered immediately through centrifugation and the final clear supernatants were then collected; analyzed through UV-Vis spectroscopy and compared their respective absorbance maxima with the raw dye solution so as to determine the respective residual dye concentrations.

Section S6:

Determination of maximum uptake capacity along with its associated adsorption isotherm study:

In this experiment we have prepared batch of ten different concentrations of RBand XO solution form 100 ppm to 1000 ppm with each of which have a difference of 100 ppm by dilution of high concentrated stock solutions. Each 10 ml of the batch solutions having varying concentrations from 100 ppm to 1000 ppm was treated with equal amount of VBT-POP material; 4 mg for all RB batch and 8 mg for all XO batch respectively. Solutions were stirred at 1200 rpm at room temperature in a loosely caped glass vial under air for 24 h so as to reach respective batch equilibrium. 2 ml aliquots from each of the respective mixtures of RB and XO batch were collected from the system; filtered through centrifugation so as to make adsorbent free; and the clear supernatants were then collected; analyzed through UV-Vis spectroscopy and compared their respective absorbance maxima with the respective raw dye solution so as to determine the respective residual dye concentrations.

Section S7:

Influence of Temperature in the adsorption Study:

In this experiment we have prepared batch of seven 500 ppm 10 mL RB solution. Each 10 ml of the batch solutions was treated with 8 mg VBT-POP material and solutions were stirred at 1200 rpm at maintained varying temperature form 273K to 333K by a difference of 10K with each other, in a loosely caped glass vial for 30 minutes under air. The temperature was maintained with a tolerance of ± 1K from the target. 2 ml aliquots from each of the respective mixtures of RB was collected from the system; filtered through centrifugation so as to make adsorbent free; and the clear supernatants were then collected; analyzed through UV-Vis spectroscopy and compared their respective absorbance maxima with the respective raw dye solution so as to determine the respective residual dye concentrations. The similar procedure was followed for the XO solution by adding of 16 mg VBT-POP material instead of 8 mg as that was used in RB.

Section S8:

Influence of pH in the adsorption Study:

Like previous here also we did batch experiment studies by preparing seven 500 ppm 10 mL RB solution. The solutions are then added with very dilute HCL/NaOH so as to make a pH series from 4 to 10 each of which is with a difference of 1 with a tolerance of ± 0.05 from the target pH. Each 10 ml of the batch solutions was treated with 8 mg VBT-POP material and solutions were stirred at 1200 rpm at RT, in a loosely caped glass vial for 30 minutes under air. 2 ml aliquots from each of the respective mixtures of RB was collected from the system; filtered through centrifugation so as to make adsorbent free; and the clear supernatants were then collected; analyzed through UV-Vis spectroscopy and compared their respective absorbance maxima with the respective raw dye solution so as to determine the respective residual dye concentrations. The similar procedure was followed for the XO solution by adding of 16 mg VBT-POP material for pH series 6-12.

Table –S1:

Necessary minimum working part of PFO and Elovich equation		
Kinetic Model	**Kinetic Equation**	**Remarks**
Lagergren Pseudo first order equation:	$\log(q_e\text{-}q_t) = \log q_e - \frac{K_1}{2.303} t$ or, $\ln(q_e\text{-}q_t) = \ln (q_e) - k_1 t$	k_1 is the PFO rate constant (unit min^{-1}). In most cases in the literature, the PFO equation doesn't fit well for the whole range of contact time and is generally applicable over the initial 20 to 30 minutes of the sorption process.
Elovich equation:	$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t)$ Or, $q_t = \beta \ln (\alpha \beta) + \ln(t)$	$\alpha$is the initial sorption rate ($mg\ g^{-1}\ min^{-1}$) and β is the desorption constant ($g\ mg^{-1}$) during any one experiment.

Table –S2

Various evaluating parameters of Kinetic study		
Parameters	**RB**	**XO**
R^2 value	0.9998	0.9997
q_e ($mg\ g^{-1}$)	666.666	320.512
K_2($g\ mg^{-1}\ min^{-1}$)	0.002045	0.004413
r ($k_2q_e^2$) ($mg\ g^{-1}\ min^{-1}$)	909.09	452.49
K_d (mL/g)	1.33×10^6	1.89×10^4

Table –S3

Necessary working part of Freundlich and Temkin adsorption isotherm model		
Isotherm Model	**Isotherm Equation**	**Remarks**
Freundlich model:	$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e$	K_F (mg/g)(L/mg)or (mg/g) is the Freundlich constant, and n corresponds to the maximum adsorption capacity and maximum adsorption intensity. The K_F and n are calculated from the plot of lnQe against lnCe.The magnitude of the exponent 1/n smaller than one gives an indication of favourable adsorption or n >1 represented the same. This model typically indicates the isothermal adsorption in a special case for heterogeneity of the adsorbent surface, heterogeneous surface energy and the possibility of the formation of more than one adsorbate layer on the surface. However, $K_F$and n are parameters characteristic of the sorbent-sorbate system, which must be determined by data fitting.
Temkin model	q_e= B $\ln A_T$ + B $\ln C_e$	The Temkin isotherm, which assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage. The Temkin model

		constants, (A_T) is the equilibrium binding constant, and (B) is the Temkin constant being estimated from the slope and intercept of the plots of q_e against ln C*e*.

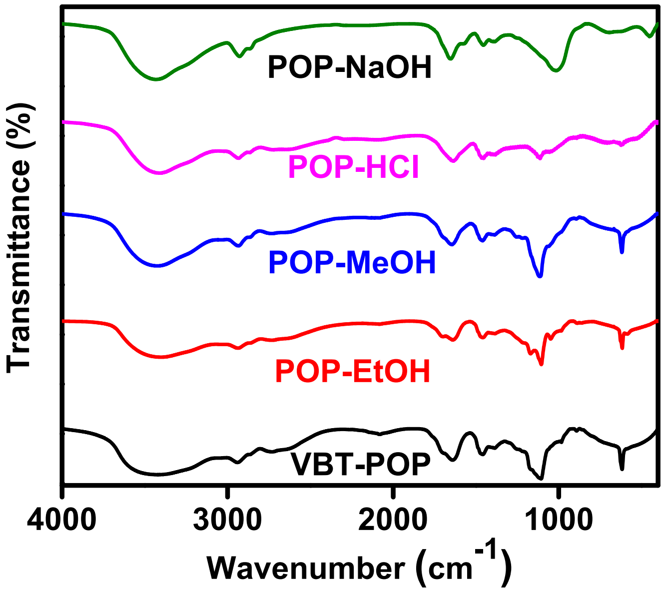


Figure S1: FT-IR spectra of VBT-POP after prolong sonication with different strong solvents.

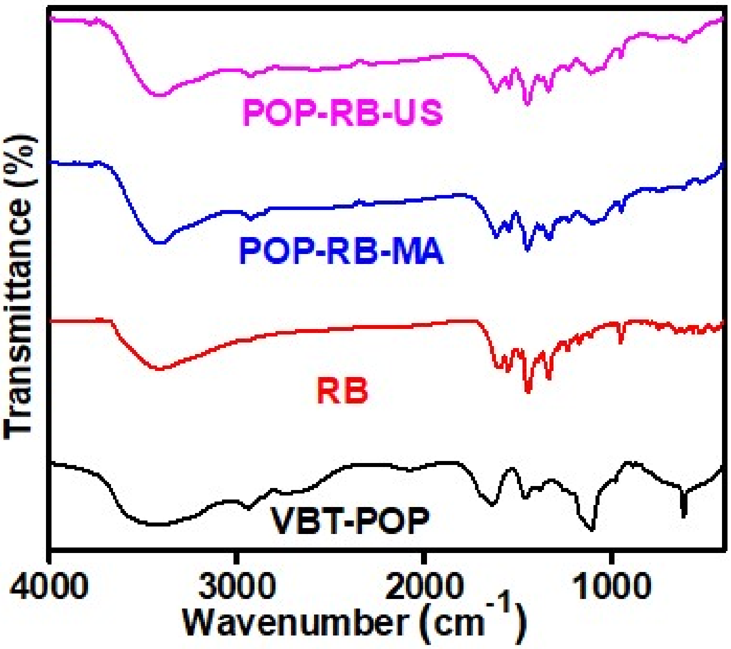


Figure S2: FT-IR analysis of VBT-POP after adsorption of RB under MA and US.

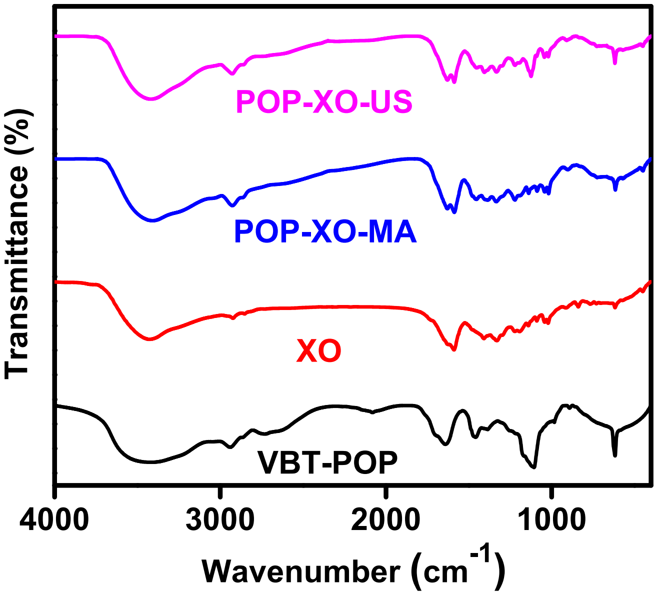


Figure S3: FT-IR analysis of VBT-POP after adsorption of XO under MA and US.

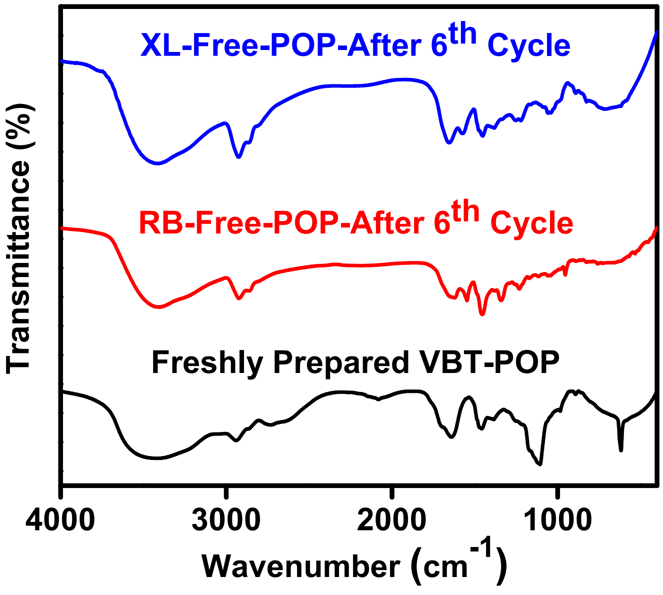


Figure S4: FT-IR analysis of VBT-POP after 6th cycle post absorptive removal of RB and XO.

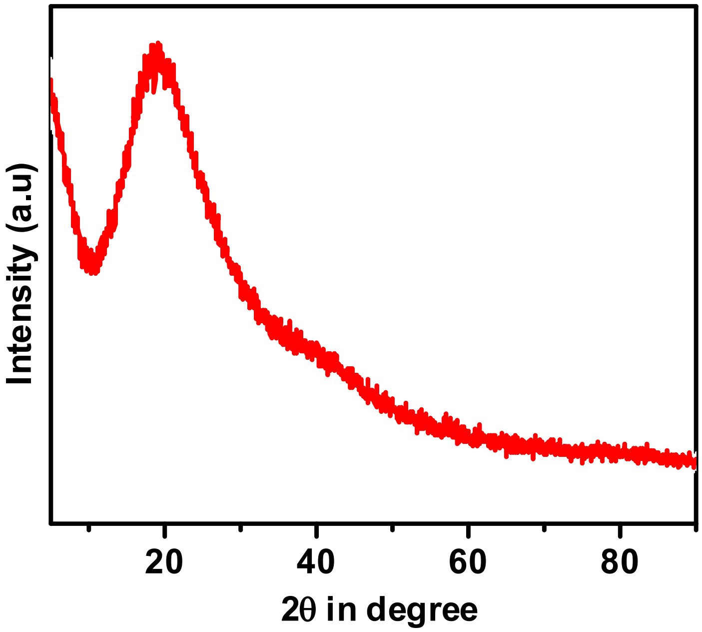


Figure S5: WA PXRD analysis of the VBT-POP.

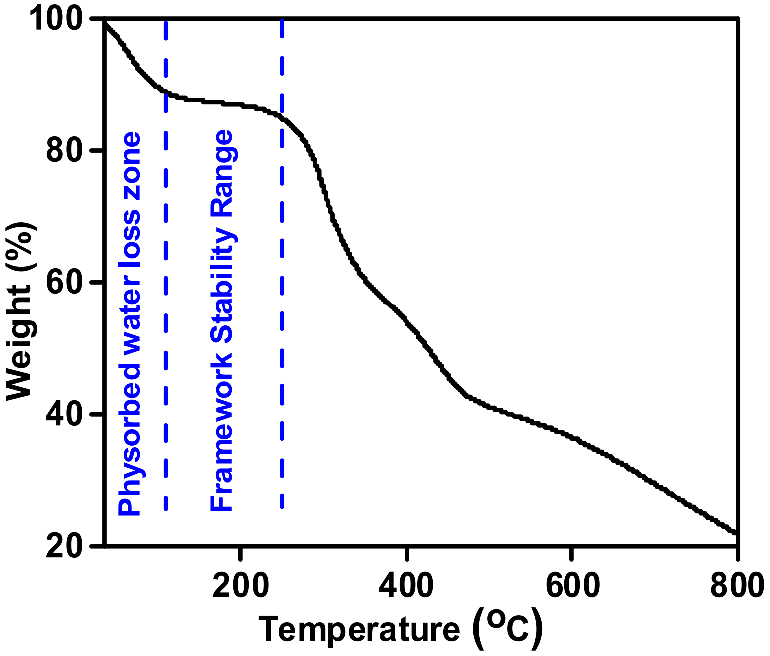
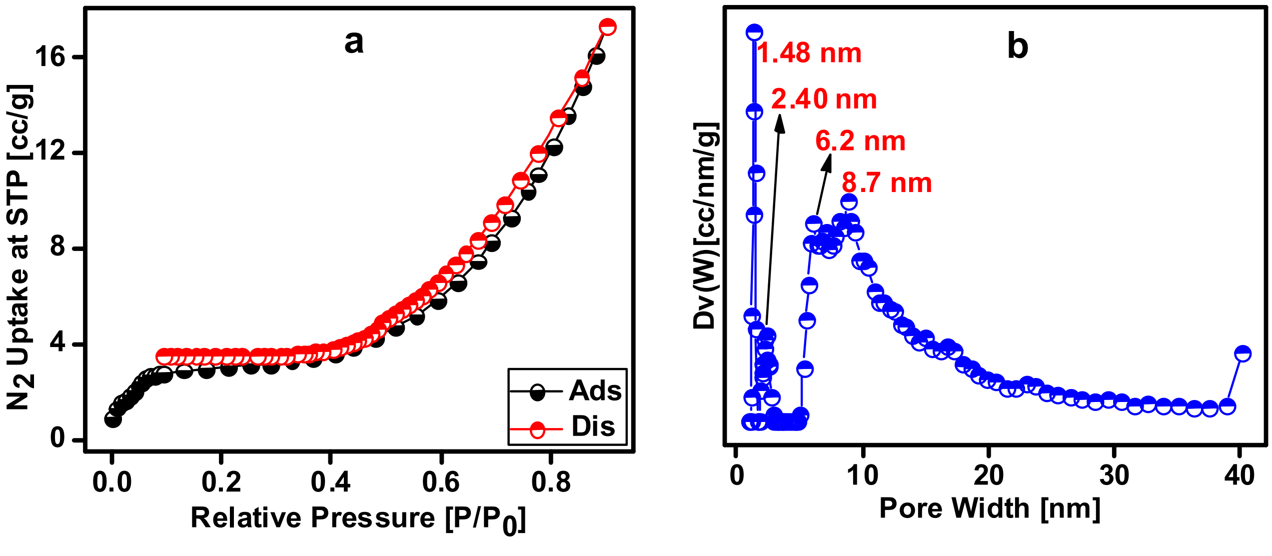


Figure S6: Thermo gravimetric analysis curve of VBT-POP.



FigureS7: BET isotherm of VBT-POP (a) and its corresponding PSD curve (b).

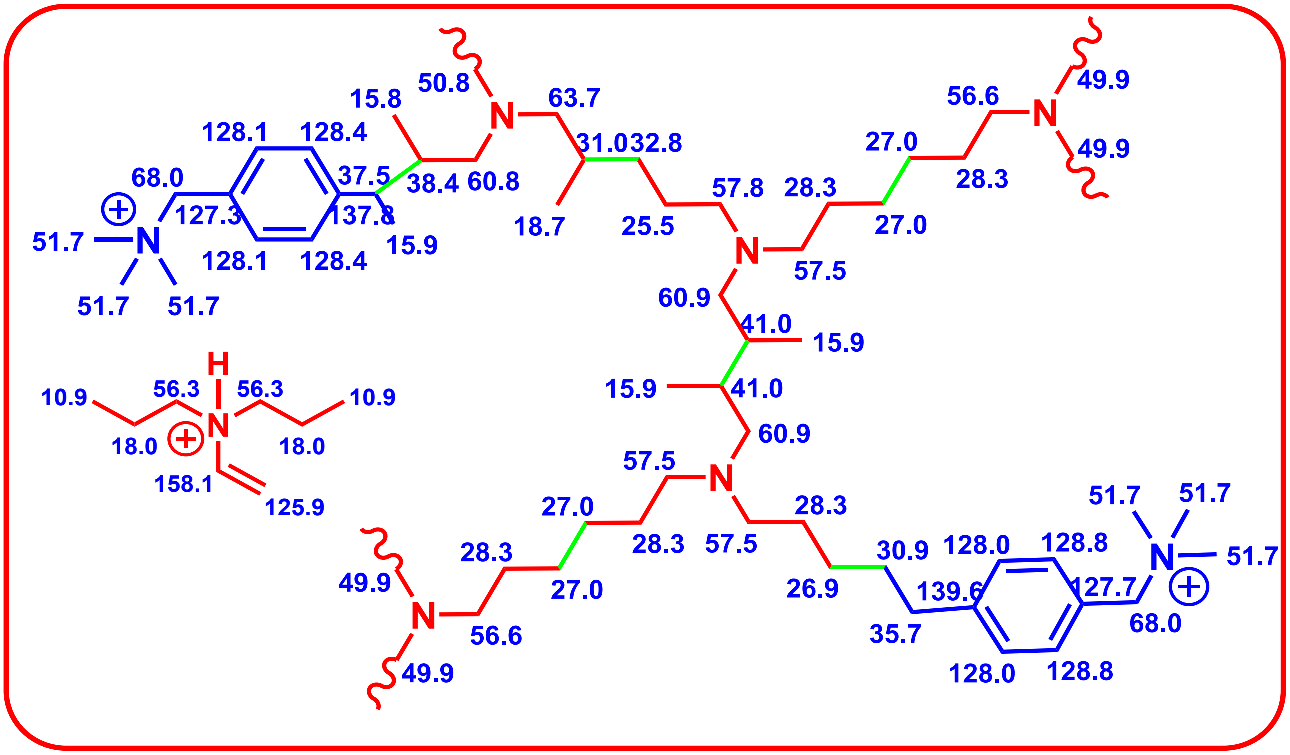


Figure S8: Possible ideal theoretical chemical shits of various carbon atoms of VBT-POP.

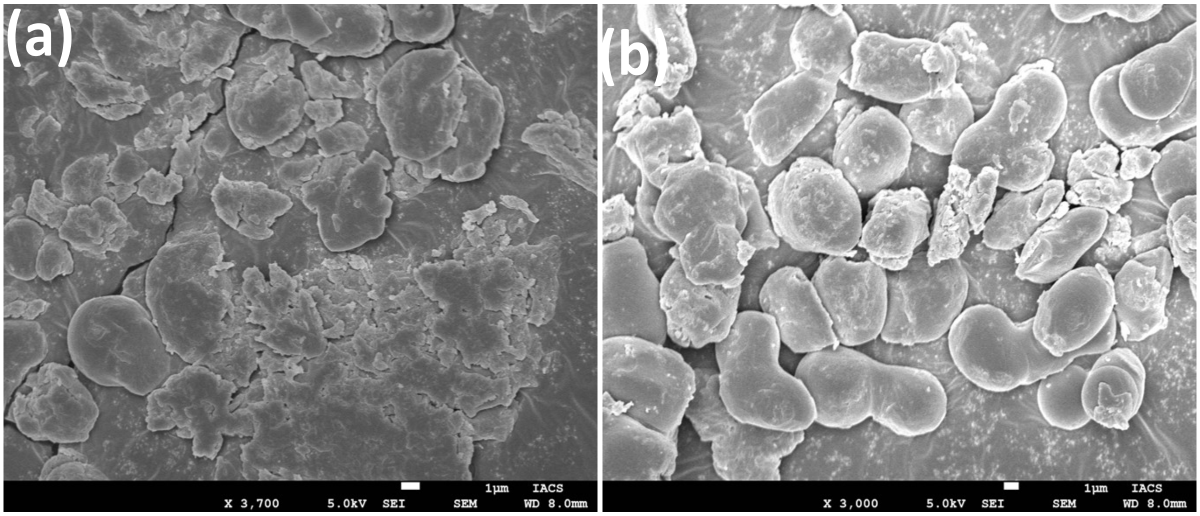
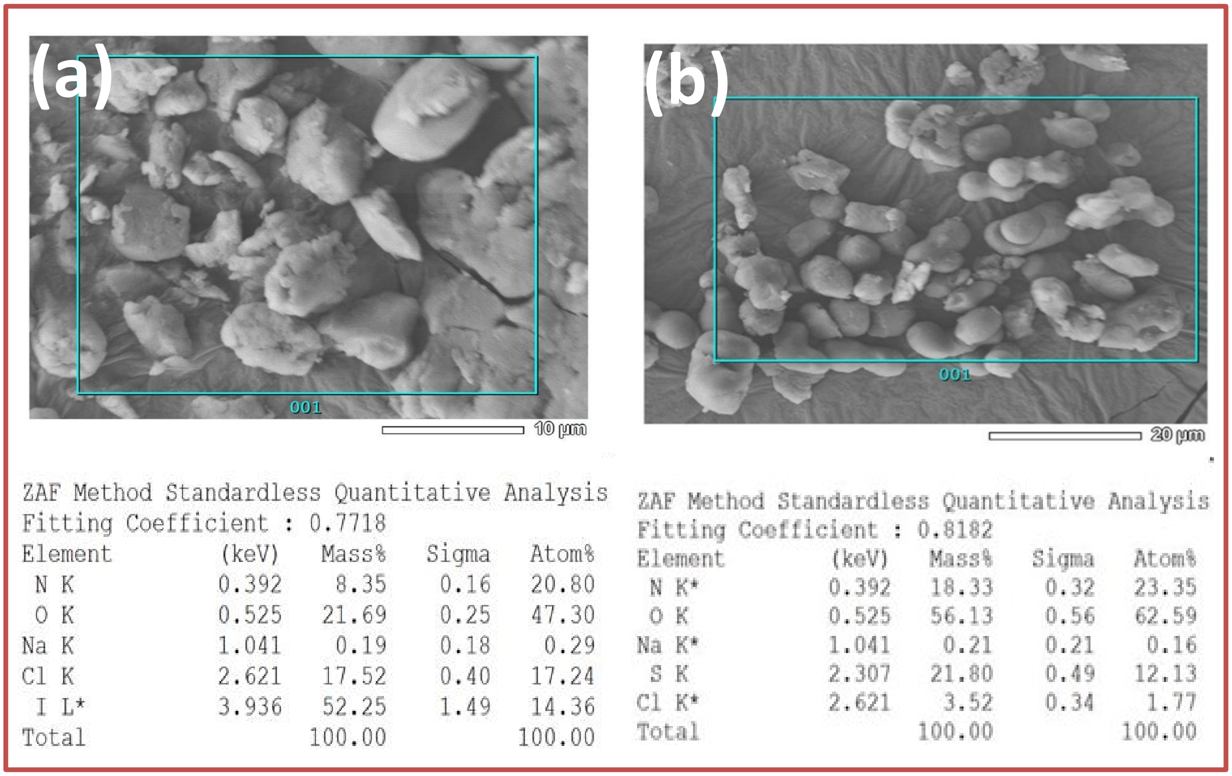


Figure S9: SEM images of VBT-POP after adsorption of RB (a) and XO (b).



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ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.7718
Element         (keV)    Mass%   Sigma   Atom%
 N K            0.392     8.35    0.16   20.80
 O K            0.525    21.69    0.25   47.30
Na K            1.041     0.19    0.18    0.29
Cl K            2.621    17.52    0.40   17.24
 I L*           3.936    52.25    1.49   14.36
Total                   100.00          100.00
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ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.8182
Element         (keV)    Mass%   Sigma   Atom%
 N K*           0.392    18.33    0.32   23.35
 O K            0.525    56.13    0.56   62.59
Na K*           1.041     0.21    0.21    0.16
 S K            2.307    21.80    0.49   12.13
Cl K*           2.621     3.52    0.34    1.77
Total                   100.00          100.00
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Figure S10: SEM-EDS analysis images of VBT-POP after adsorption of RB (a) and XO (b).

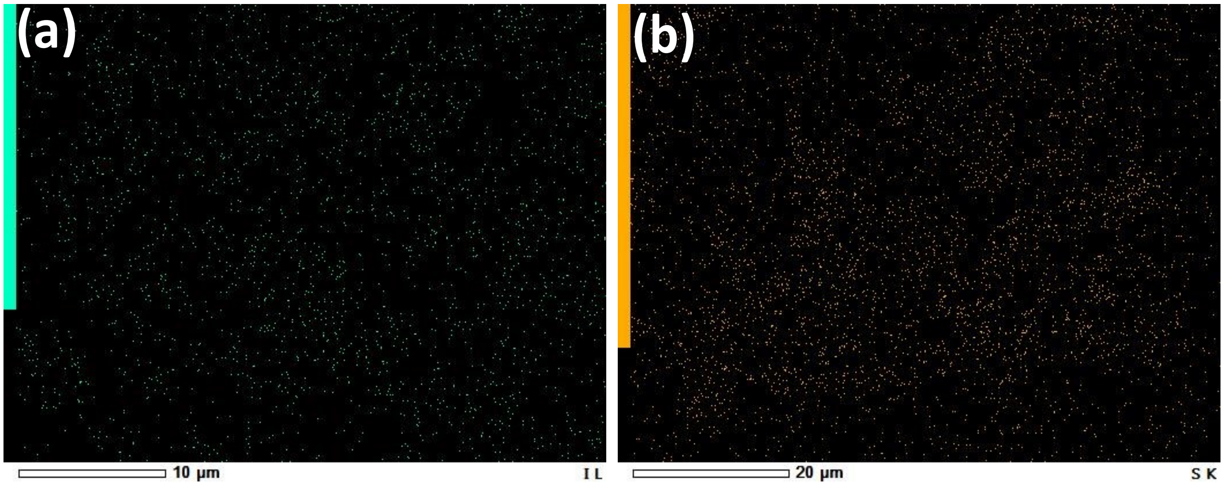


Figure S11: Elemental mapping of VBT-POP after adsorption of RB (a, iodine) and XO (b, sulfur).

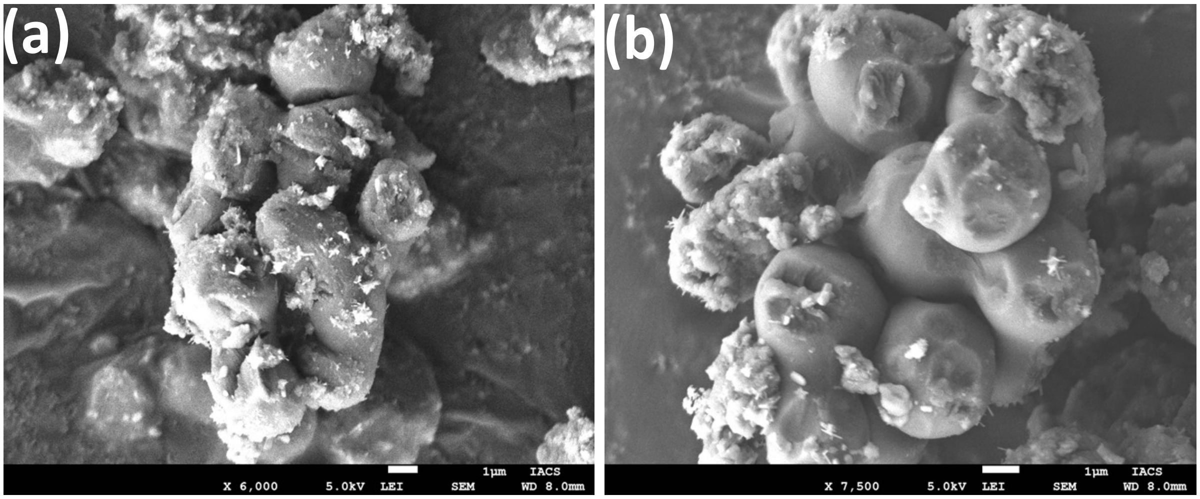


Figure S12: SEM images of VBT-POP after 6th cycle post absorptive removal of RB (a) and XO (b).

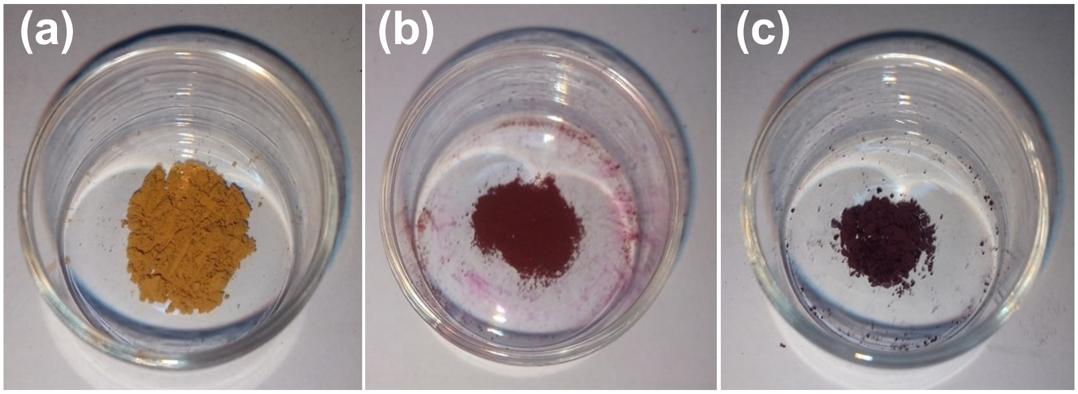


Figure S13: Digital images of VBT-POP (a) that of RB adsorbed (b) and XO (c).

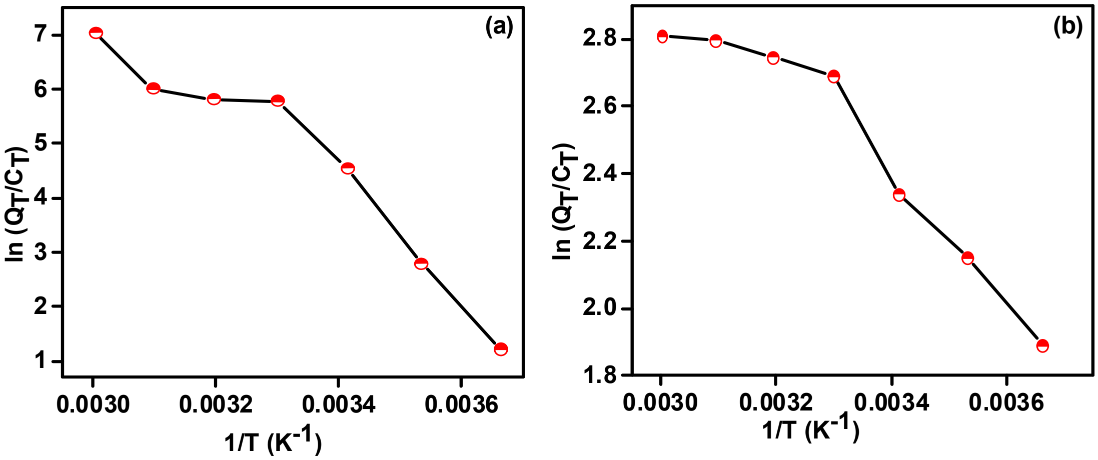


Figure S14: Represents linear regression by fitting of the temperature dependent dye uptake data withVan't Hoff model for a) RB and b) XO.

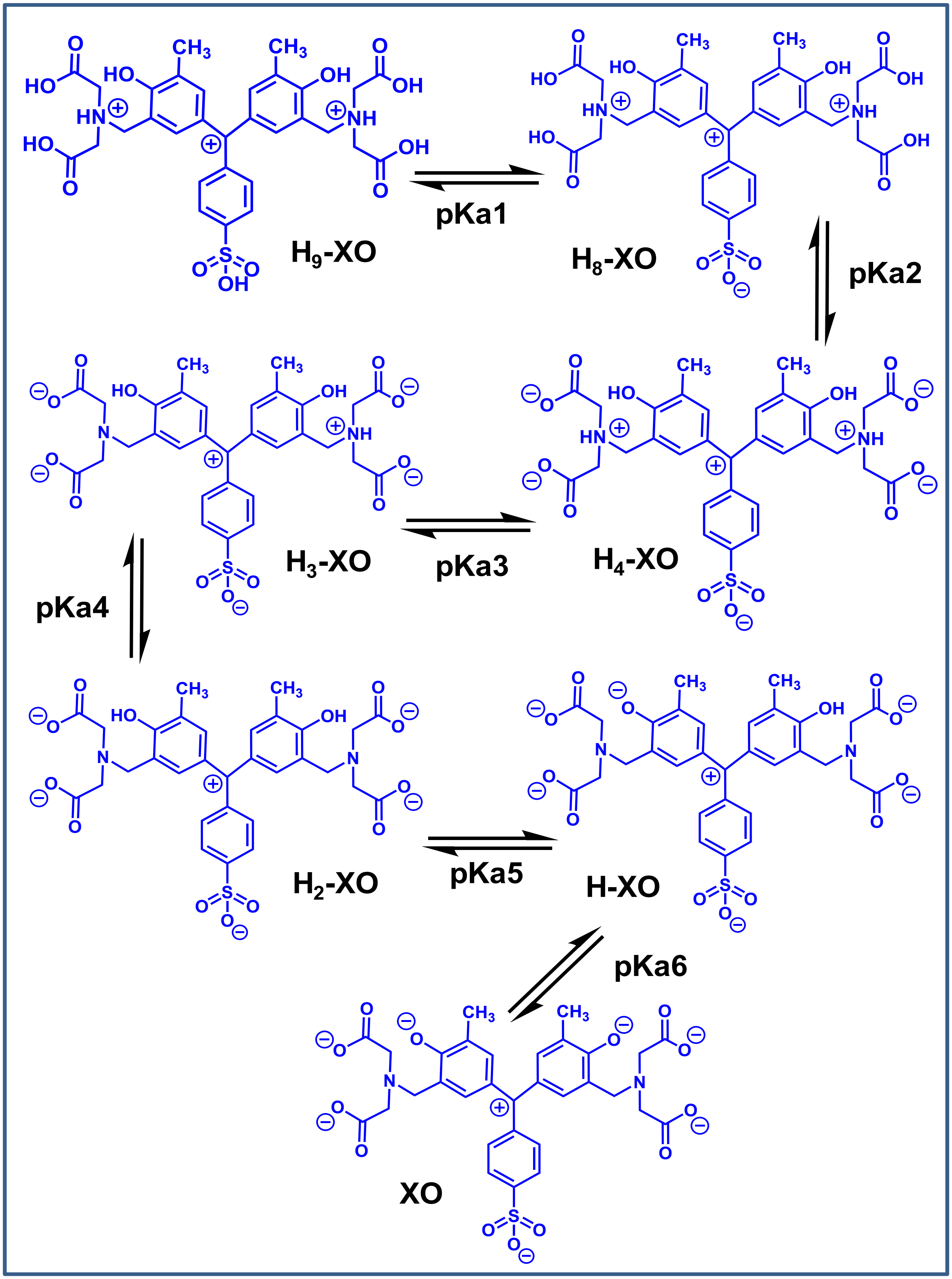


Figure S15: Represents successive protonation of XO along with its associated pKa's.

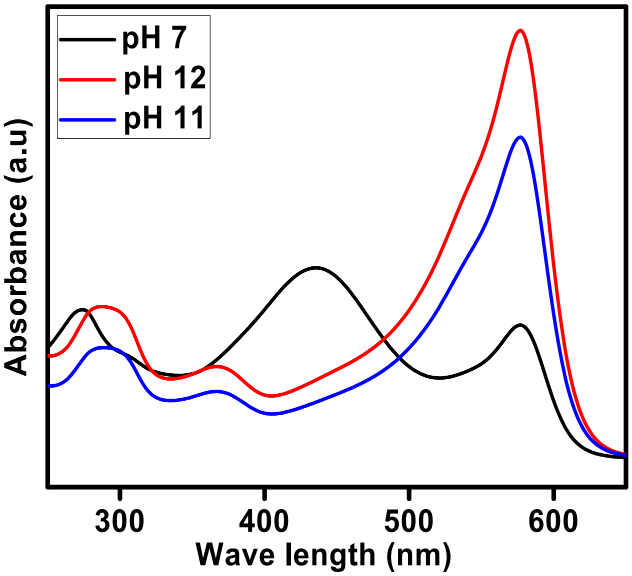
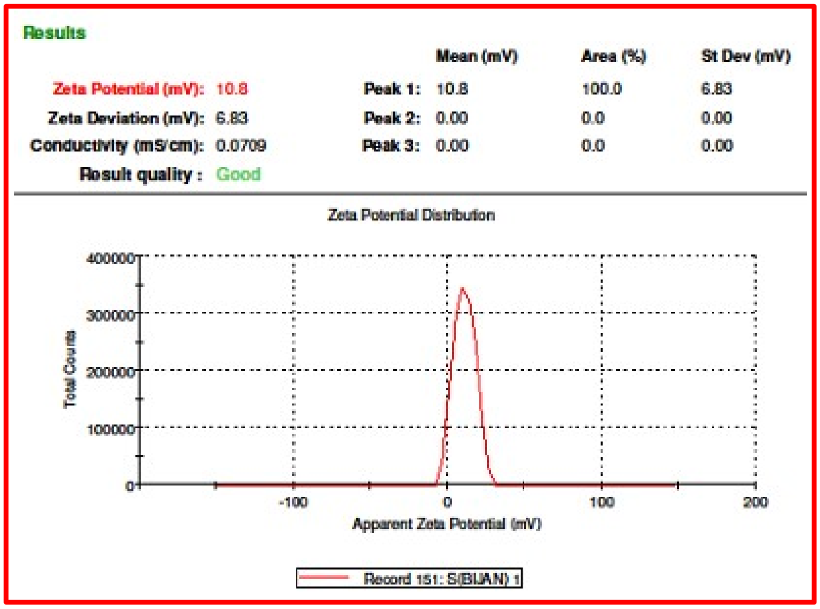


Figure S16: Represents pH dependent change of UV-Vis spectral pattern of XO along with its associated characteristics $\lambda_{\max}$.



Results

			Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV):	10.8	Peak 1:	10.8	100.0	6.83
Zeta Deviation (mV):	6.83	Peak 2:	0.00	0.0	0.00
Conductivity (mS/cm):	0.0709	Peak 3:	0.00	0.0	0.00
Result quality :	Good				

Figure S17: Represents the result obtained from the surface charge measurement of the VBT-POP.