

## Supplementary information

### Scalable Synthesis of Hide substance(Hs)-Chitosan(Cs)–Hydroxyapatite(HAp):A novel bio-composite from industrial wastes and its efficiency in dye removal.

Sandipan Chatterjee<sup>†\*</sup>, Arka Gupta<sup>†#</sup>, Tamal Mohanta<sup>±</sup>, Rangeet Mitra<sup>†</sup>, Debasis Samanta<sup>‡</sup>,  
Asit Baran Mandal<sup>‡\*</sup>, Mousumi Majumder<sup>‡</sup>, Ritu Rawat<sup>§</sup>, Nayan R. Singha<sup>±</sup>

<sup>†</sup>RCED-Kolkata, CSIR-Central Leather Research Institute, 3/1C Matheswartala Road, Kolkata-700046, West Bengal, India.

<sup>±</sup>Leather Technology Division and Department of Polymer Science and Technology, Govt. College of Engineering and Leather technology. Block-LB 11, Sector-III, Salt Lake City, Kolkata- 700106, West Bengal, India

<sup>#</sup>Polymer Science and Technology Division, CSIR-Central Leather Research Institute. Adyar, Chennai 600020, Tamilnadu, India.

<sup>‡</sup>Material Characterization & Instrumentation and Nanostructured Material Divisions, CSIR-Central Glass and Ceramic Research Institute, 196, Raja S.C. Mullick Road, Jadvapur, Kolkata 700032, West Bengal, India.

<sup>§</sup>Squid-VSM and PLD Lab, UGC-DAE Consortium for Scientific Research, Indore centre, University Campus, Khandwa Road, Indore 452017, Madhya Pradesh, India.

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\*Corresponding author: **Dr. Sandipan Chatterjee**  
Scientist, Regional Centre for Extension and Development  
(Assistant Prof. AcSIR, CSIR, India)

CSIR-Central Leather Research Institute  
3/1C, Matheswartala Road, Kolkata 700 046

Email: [sandipan@clri.res.in](mailto:sandipan@clri.res.in), [sandipan.clri@gmail.com](mailto:sandipan.clri@gmail.com)

Phone: +91 33 2329 2381, Fax: +91 33 2329 6046

\*Corresponding author: **Prof. Dr. Asit Baran Mandal**

(Former Director and Outstanding Scientist, CSIR-Central Leather Research Institute, Chennai, India)

INAE Distinguished Professor, CSIR-Central Glass and Ceramic Research Institute, 196, Raja S.C. Mullick Road, Jadavapur, Kolkata 700032

Email : [abmandal@hotmail.com](mailto:abmandal@hotmail.com); [abmandal@cgcric.res.in](mailto:abmandal@cgcric.res.in),

Phone: +91 33 2473 5829, Fax: +91 33 2473 0957

## **General characterization of the material:**

### **Solid state NMR analysis:**

The solid-state NMR experiments were performed on a Bruker Avance-III HD 400 WB NMR spectrometer (9.4 T). The <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P and <sup>15</sup>N resonance frequencies were 400.07, 100.61, 161.95 and 40.54 MHz respectively. Samples were packed in a 4-mm-diameter zirconia rotor with a Kel-F cap. All the NMR spectra of the samples were recorded at room temperature using a double resonance 4 mm MAS probe. <sup>13</sup>C cross polarization/total sideband suppression (CP/TOSS) experiment was performed at a spinning speed of 7 kHz to get sideband free spectrum. Typically, 3k scans were acquired with a relaxation delay of 4s. For <sup>15</sup>N, CPMAS experiments carried out at a spinning speed of 5 kHz. 12k scans were employed with a relaxation delay of 5s to obtain good signal to noise ratio. For all the CP experiments contact time of 3 ms with a linear ramp on the <sup>1</sup>H contact pulse (50% slope) and <sup>1</sup>H 90° pulse length of 4 μs were employed. In the case of <sup>31</sup>P, single pulse excitation with proton decoupling experiment at a spinning speed of 5 kHz was carried out for 64 scans, recycle delay of 4s and <sup>31</sup>P 90° pulse length of 4 μs. SPINAL-64 decoupling sequence was used to decouple protons during the <sup>13</sup>C/<sup>15</sup>N/<sup>31</sup>P acquisition by employing radiofrequency field strength of 83 kHz. FID was subjected to an appropriate exponential multiplication function prior to Fourier transform. <sup>13</sup>C chemical shifts were referenced externally to the carbonyl signal of glycine at 176.03 ppm, <sup>15</sup>N was referenced to solid ammonium chloride at 35.9 ppm and <sup>31</sup>P was referenced to ADP at 1 ppm.

### **FTIR analysis:**

Approximately 40 mg powdered experimental sample was blended with 100 mg spectroscopic grade KBr for the preparation of pellets and FTIR spectra of the samples were taken in Shimadzu FTIR 8300 spectrophotometer with 100 scans and resolution 4 cm<sup>-1</sup>.

### **XPS spectra**

XPS analysis of composite (Hs-Cs-HAp) and HAp samples were carried out using monochromatic X-ray sources Al Kα (E = 1486.6 eV) and Mg Kα (E = 1253.6 eV) by Omicron energy analyser. Deconvolution of the superimposed peak were done using XPS peak (software version 4.1).

### **XRD analysis:**

Powder X-ray diffraction patterns were obtained using Seifert C 3000 instrument with the following operating conditions – 40kV and 30 mA with a Cu/Ni radiation at λ=1.5406. The relative intensity was recorded in a scattering range (2θ) of 10-100°.

### **Optical microscopic and SEM analysis:**

The macro structure of the material has been analysed by Novax zoom stereo microscope by Euromax Microscopen B.V. Holland. For the optical microscope study samples were dried under vacuum oven for 1.5 hr. at 105 °C followed by cooling to RT under desiccating condition prior to analysis. SEM images were taken on a FEI Quanta 200 F, using a tungsten filament doped with lanthanum hexaboride (LaB<sub>6</sub>) as an X-ray source, fitted with an ETD

detector with high vacuum mode, using secondary electrons and an acceleration tension of 10 or 30 kV. Samples were analyzed by spreading them on a carbon tape. Energy dispersive X-ray spectroscopy (EDX) was used in connection with SEM for the elemental analysis. The elemental mapping was also collected with the same spectrophotometer.

**TEM analysis:**

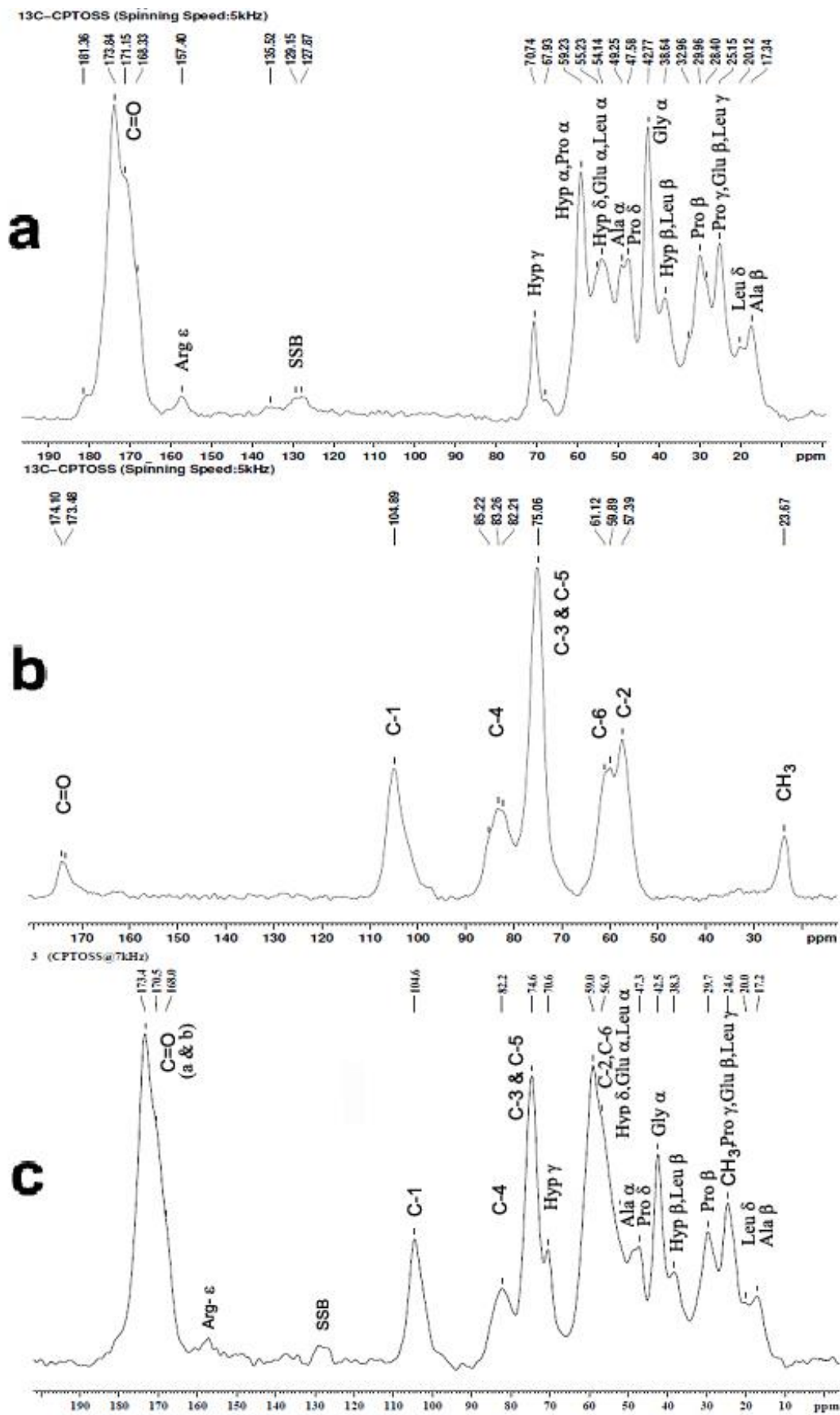
The samples for TEM analysis were prepared by mounting an ethanol-dispersed sample on a lacey carbon Formvar coated Cu grid and TEM images of the prepared samples were collected using a Jeol JEM 2100 microscope. Energy dispersive X-ray Spectrometer used for analysis for the elemental analysis and characterisation using TEM 2100 model which can be operated under 80KV to 200KV, having LAB 6 and Tungsten as a filament used for producing high intensity electron beam. Oxford detector (**EDS, Oxford Energy Max 80**) is used here for analysis under EDS Mode and by using Bright Field and Dark Field Detector for STEM images and here we are using AZtech Software of OXFORD instrument for achieving a better results.

**BET surface area and porosity analysis:**

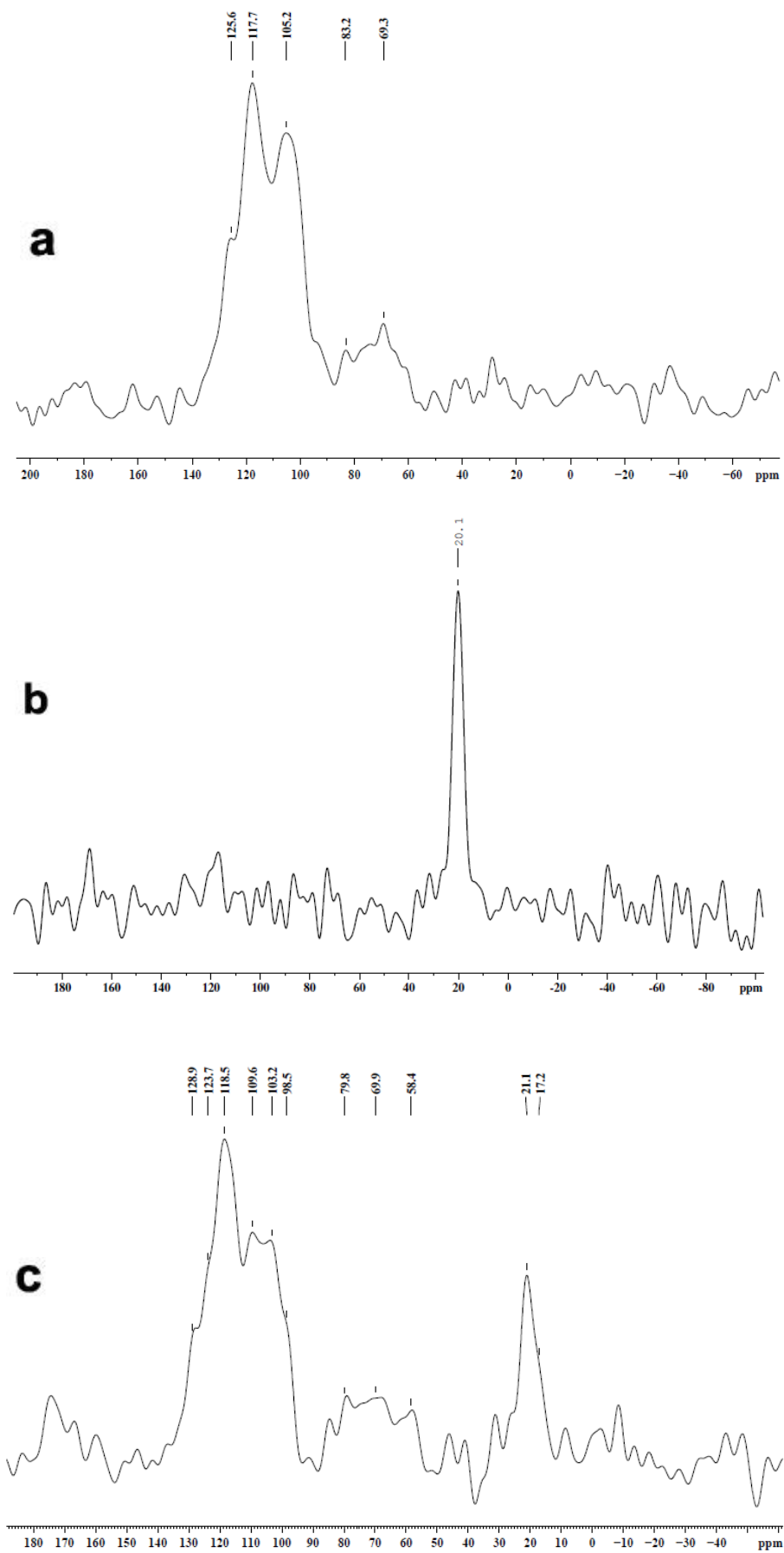
Brunauer-Emmett-Teller (BET) surface area and total pore volume of the material were obtained by measuring their nitrogen adsorption isotherm at 77 K in a surface area and porosity analyser (Quantachrome ASIQwin Autosorb Automated Gas Sorption System). Analysis of macroporous in of the material was done using Hg intrusion Quantachrome Poremaster instrument.

**TGA analysis:**

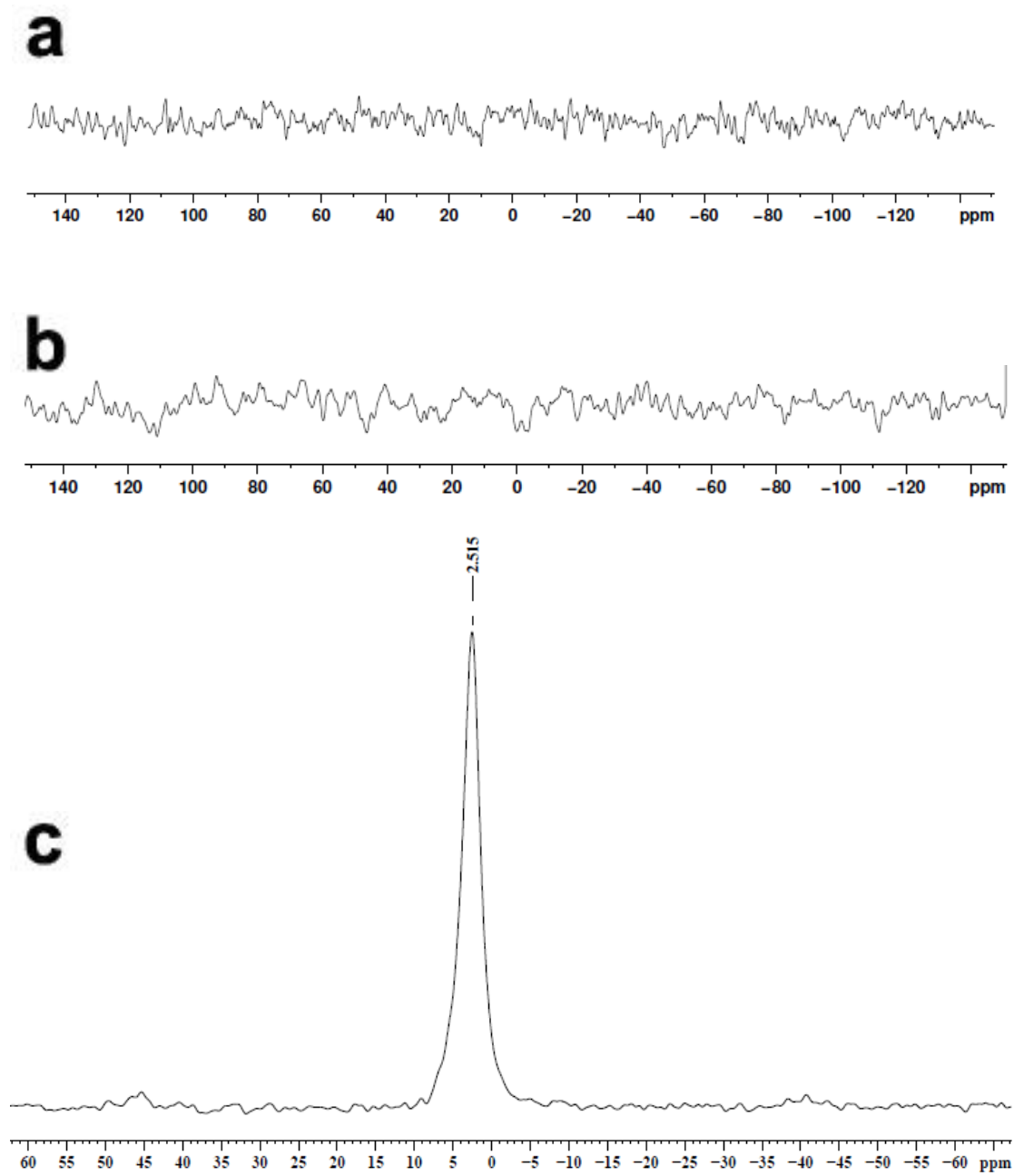
TGA of the samples were performed in TFAQ50 V 6.1 Build 181 instrument. Approximately 10 g of the each sample was encapsulated non hermetically in a platinum pan and scanned from 30 °C to 500 °C at a heating rate of 20 °C per minute under nitrogen atmosphere. Each experiment was repeated thrice for better accuracy of the result.



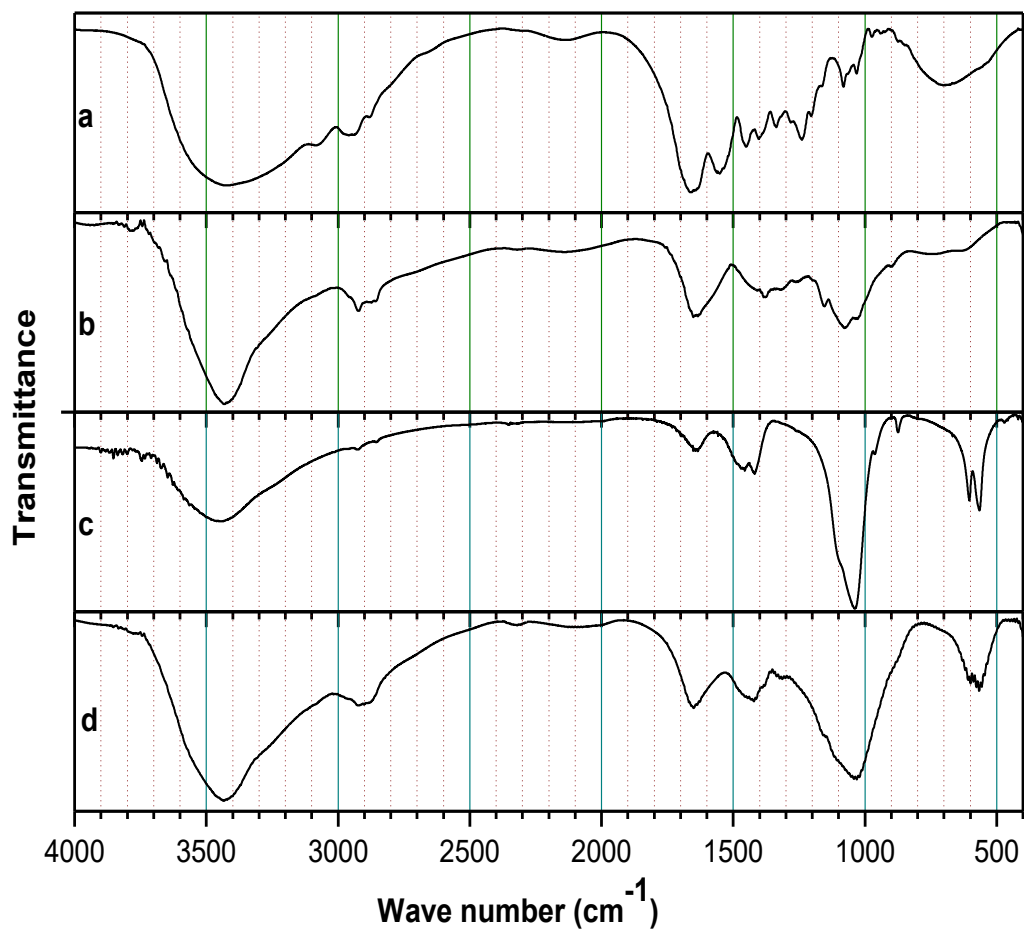
**Figure S1.** Solid state  $\text{C}^{13}$  NMR spectra of (a) Hs, (b) Cs, (c) Hs-Cs-HAp (composite)



**Figure S2.** Solid state  $N^{15}$  NMR spectra of (a) Hs, (b) Cs, (c) Hs-Cs-HAp (composite)



**Figure S3.** Solid state  $\text{P}^{31}$  NMR spectra of (a) Hs, (b) Cs, (c) Hs-Cs-HAp (composite)



**Figure S4.** FTIR spectra of the (a) Hs, (b) Cs, (c) HAp, (d) Hs-Cs-HAp.

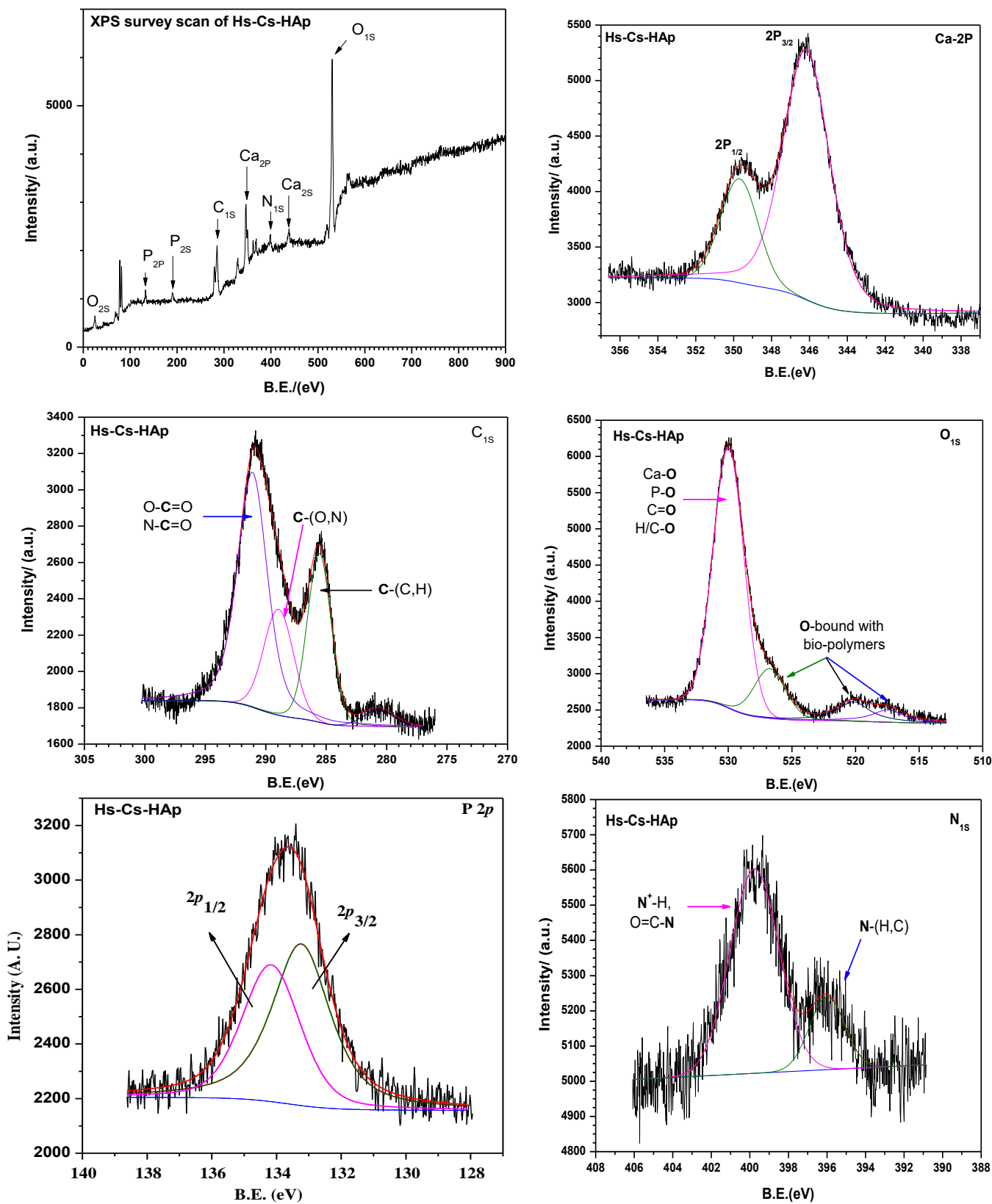


Figure S5. XPS spectra of Hs-Cs-HAp



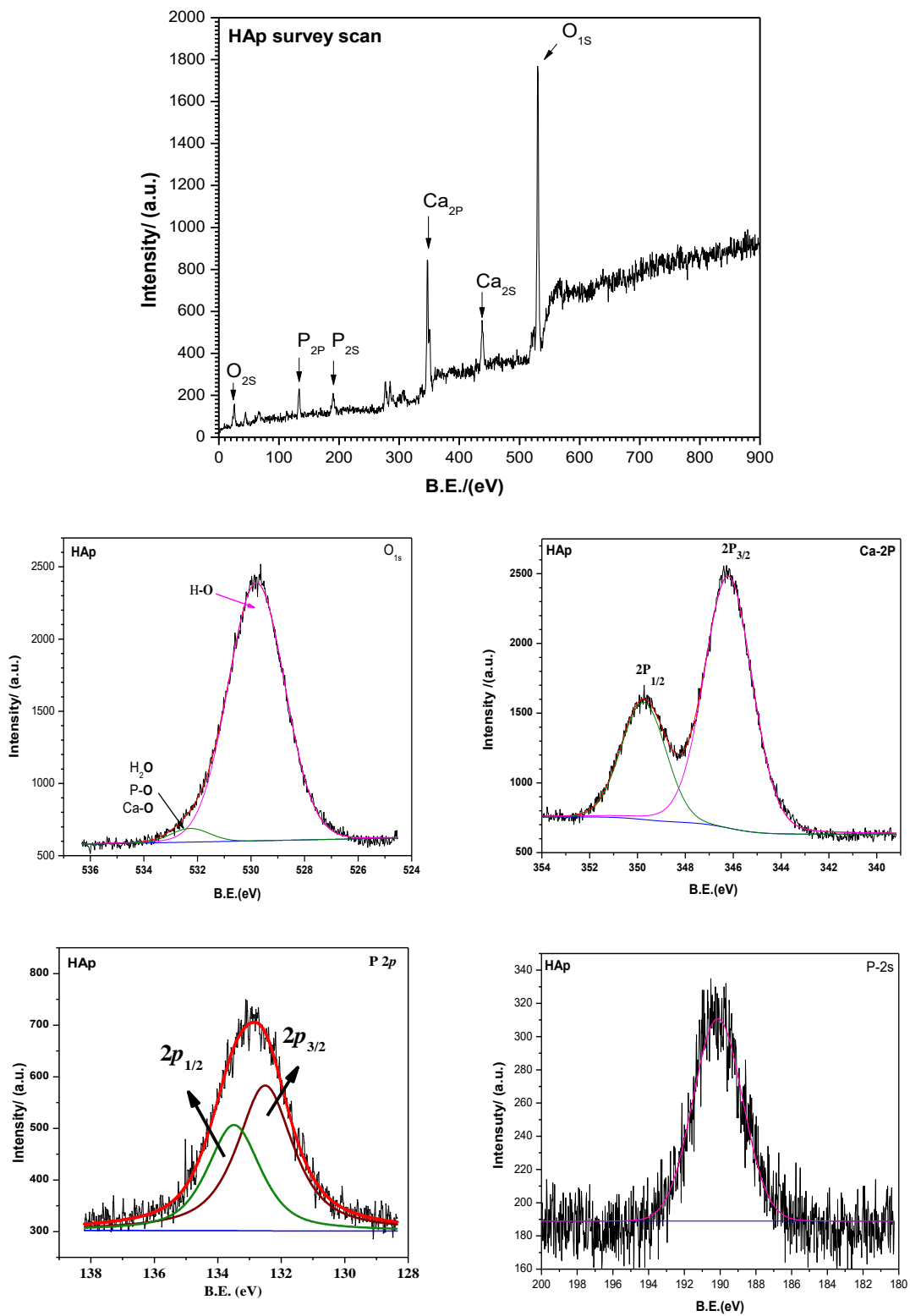


Figure S6. XPS spectra of pure HAp

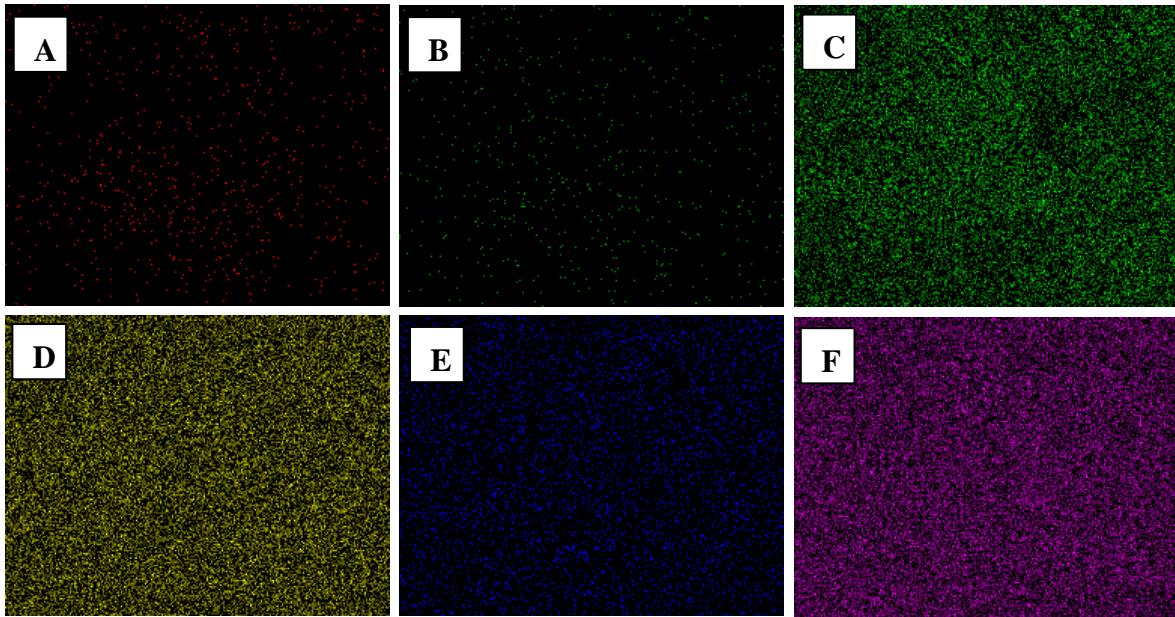
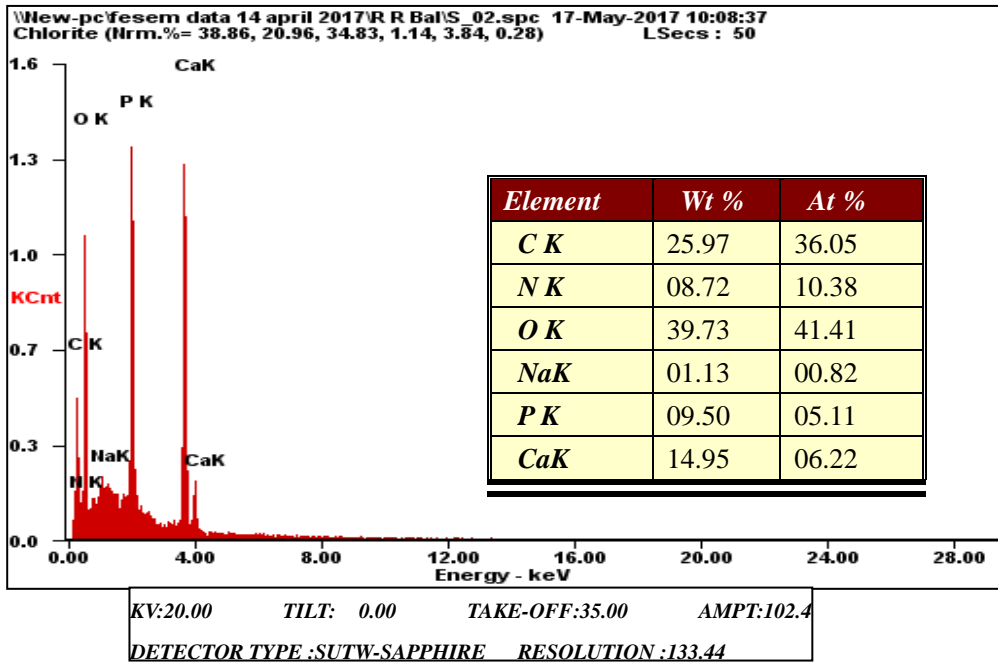
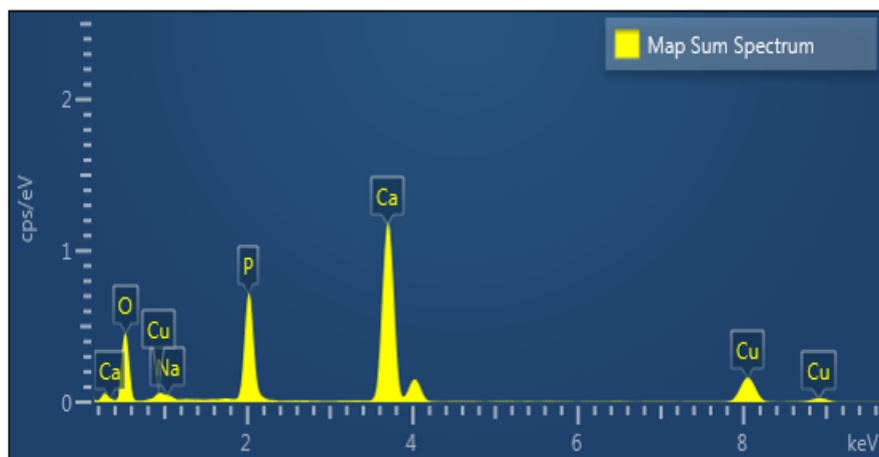
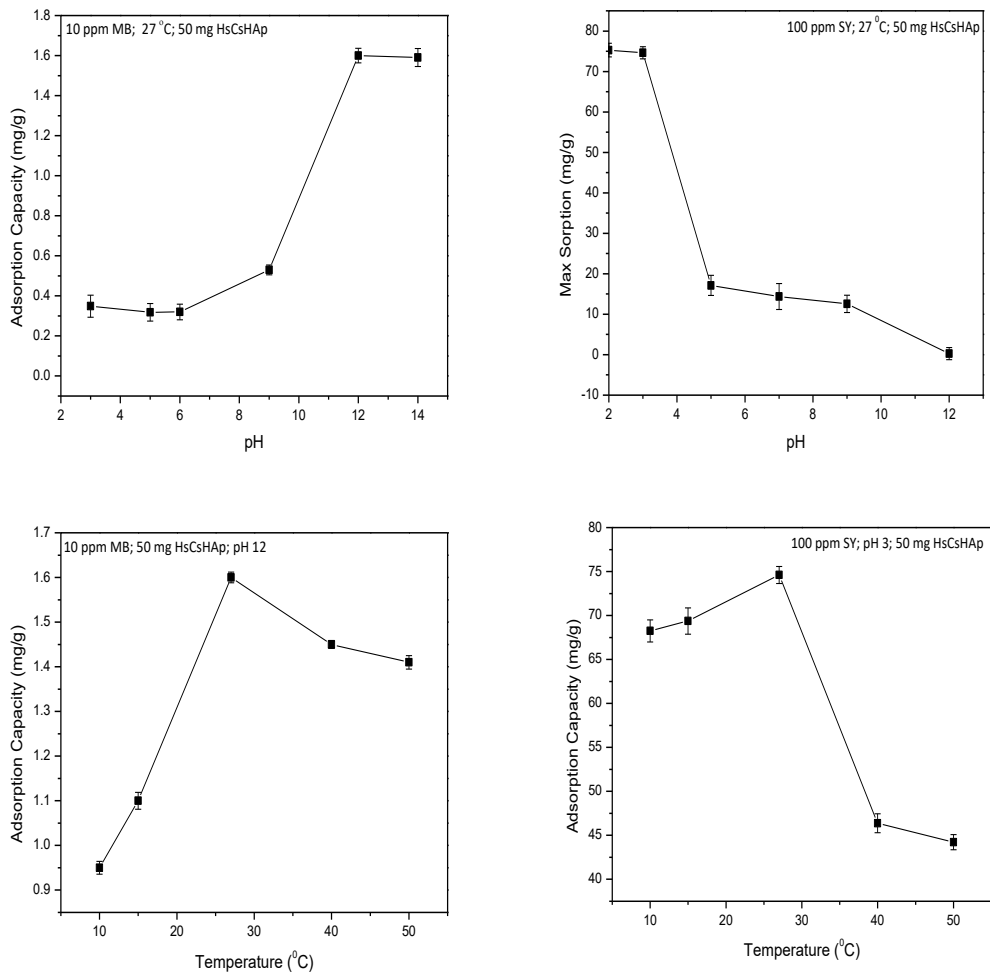


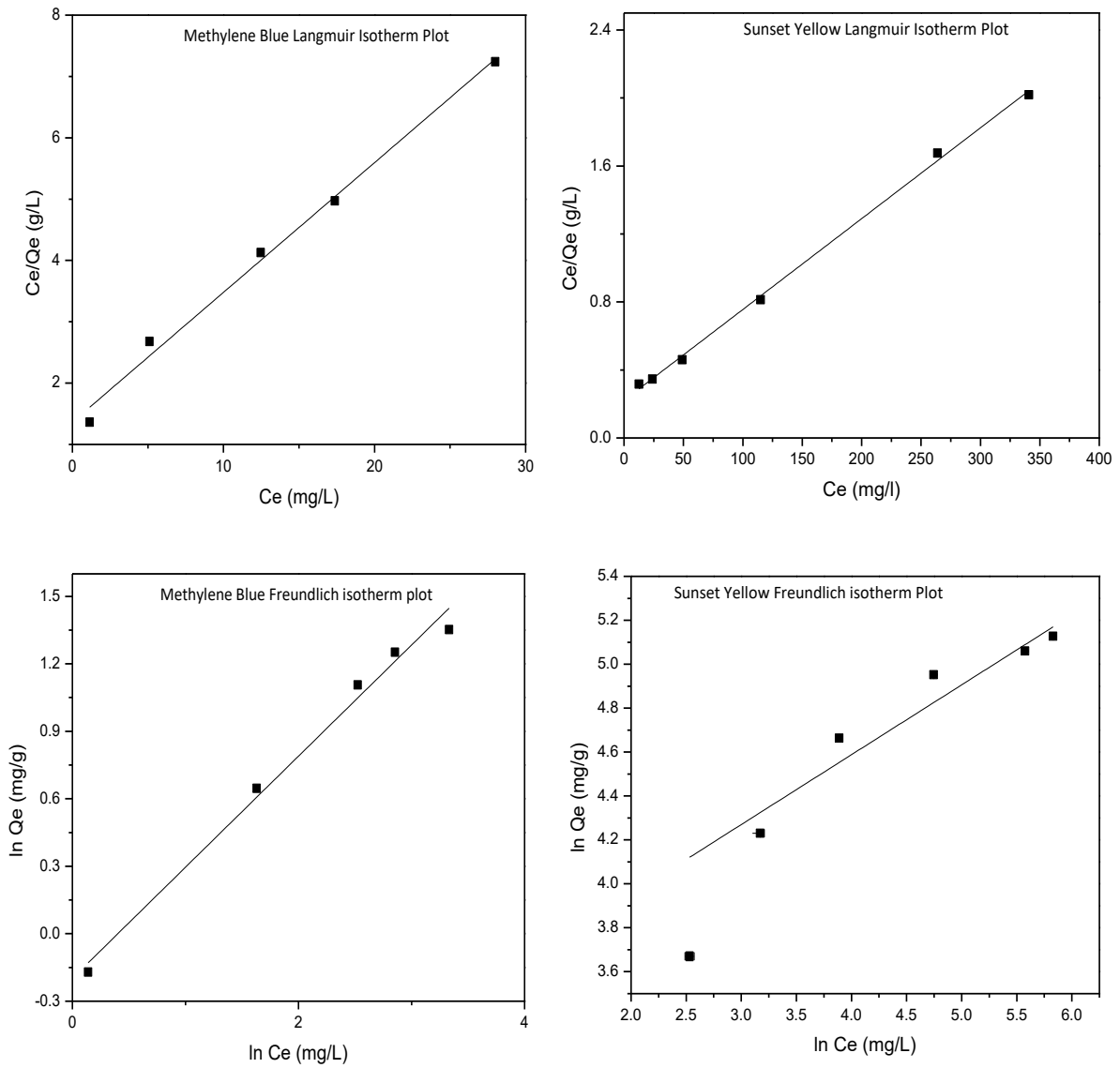
Figure S7. Elemental mapping of Hs-Cs-HAp; A: Carbon, B: Nitrogen, C: Oxygen, D: Phosphorous, E: Sodium, F: Calcium



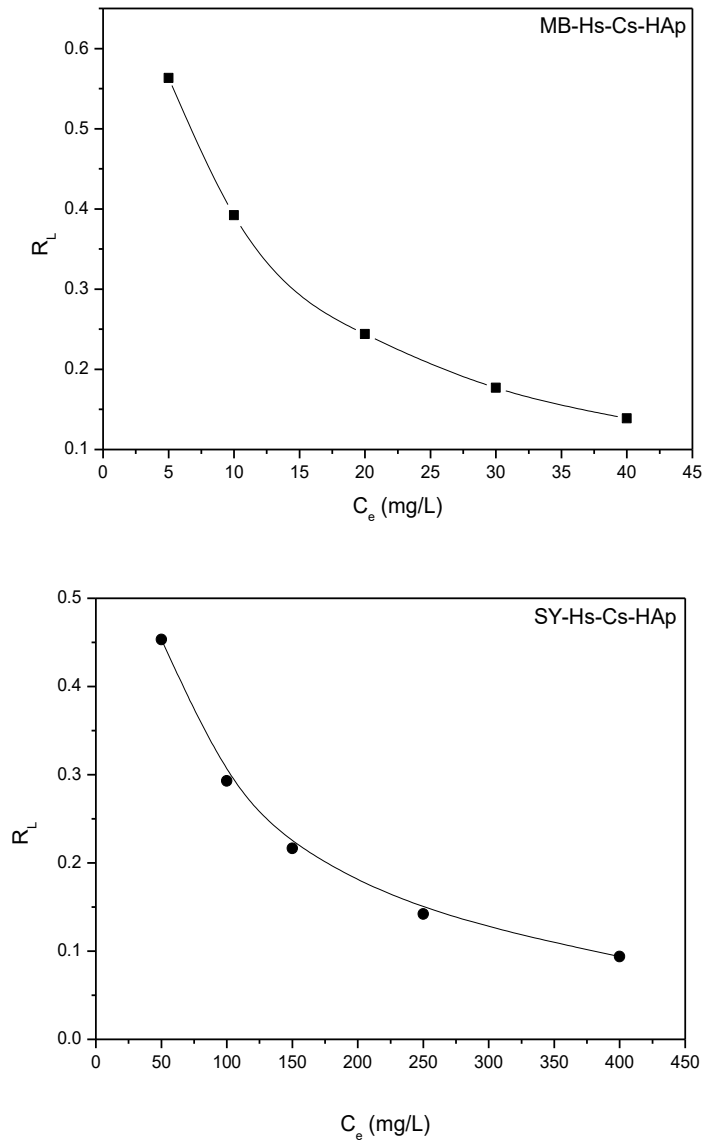
**Figure S8.** TEM EDS of rod like crystalline aggregate (Fig. 2c) found in Hs-Cs-HAp.



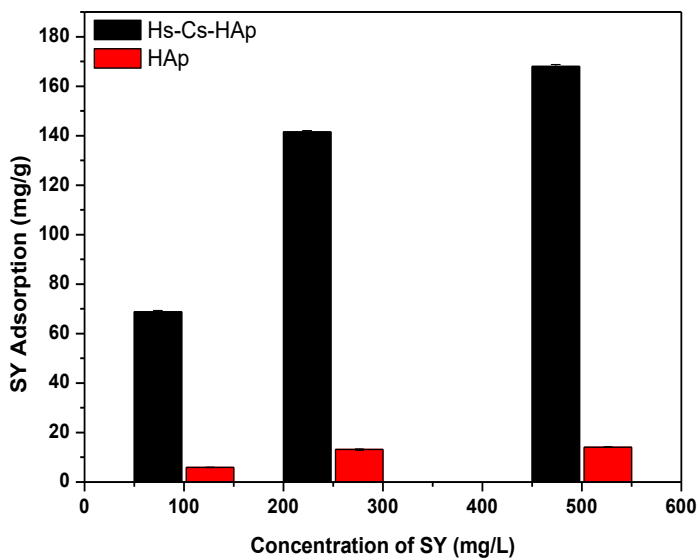
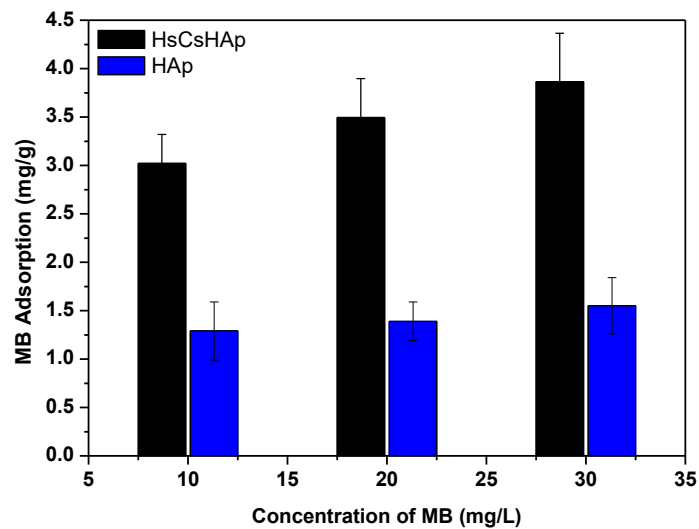
**Figure S9.** Effect of pH and temperature over MB and SY adsorption by Hs-Cs-HAp.



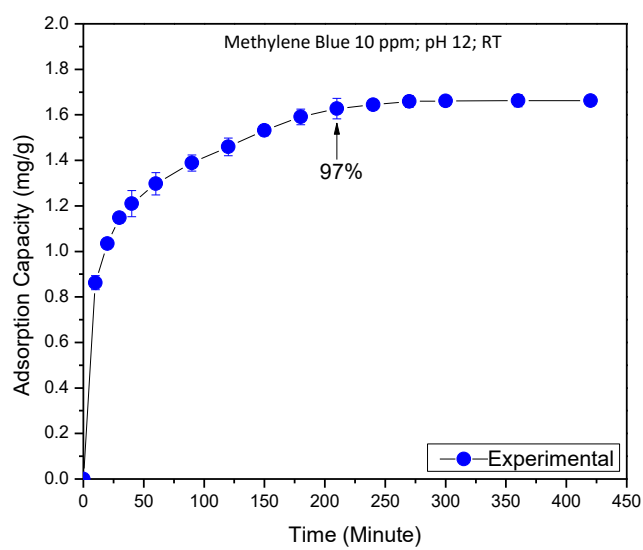
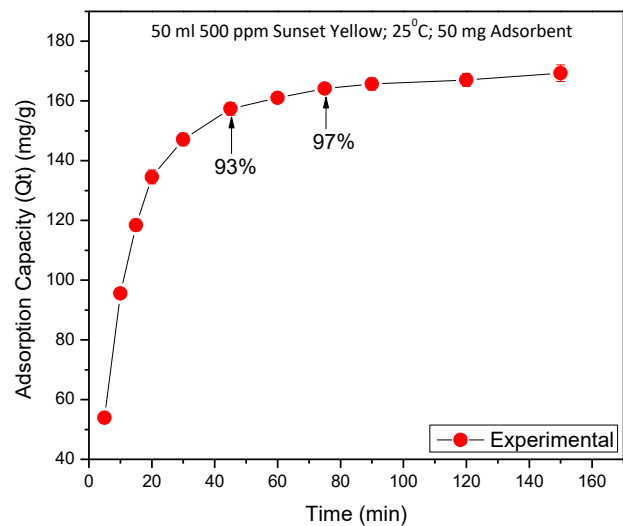
**Figure S10.** Langmuir and Freundlich isotherms plots for MB-Hs-Cs-HAP and SY-Hs-Cs-HAP adsorption system.



**Figure S11.** Calculated  $R_L$  value at different  $C_0$  for MB and SY from Langmuir isotherm.

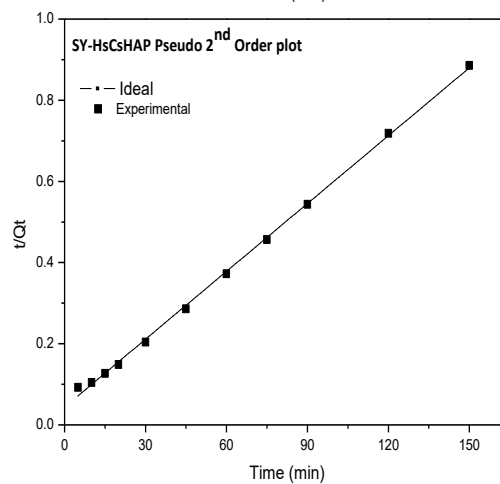
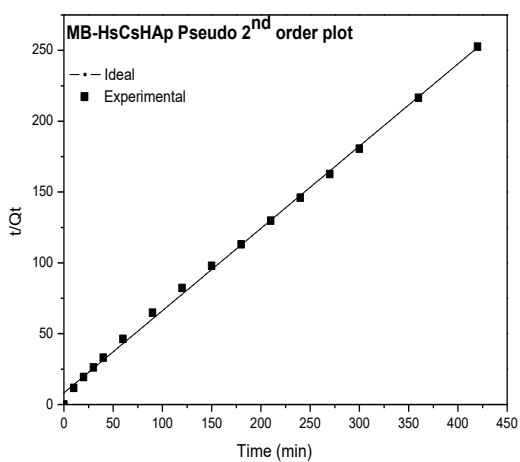
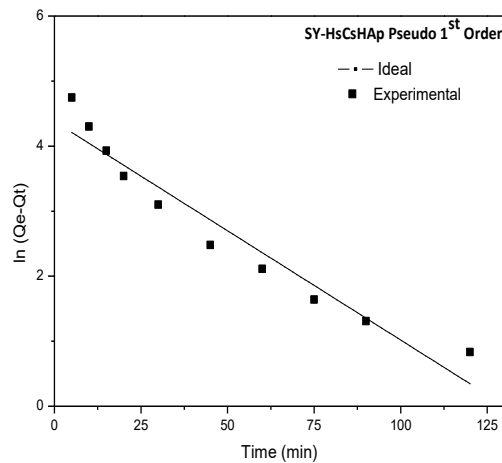
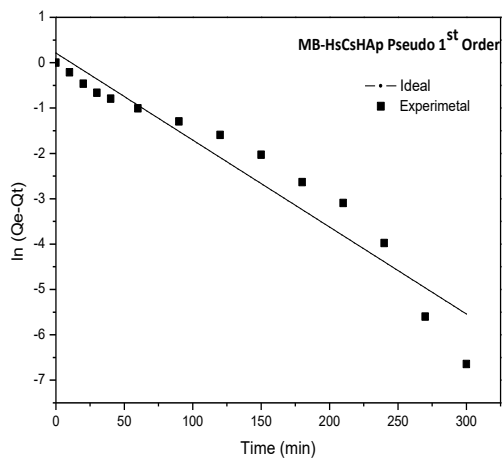


**Figure S12.** Comparison of adsorption of dyes (a) MB, (b) SY by composite and HAp.

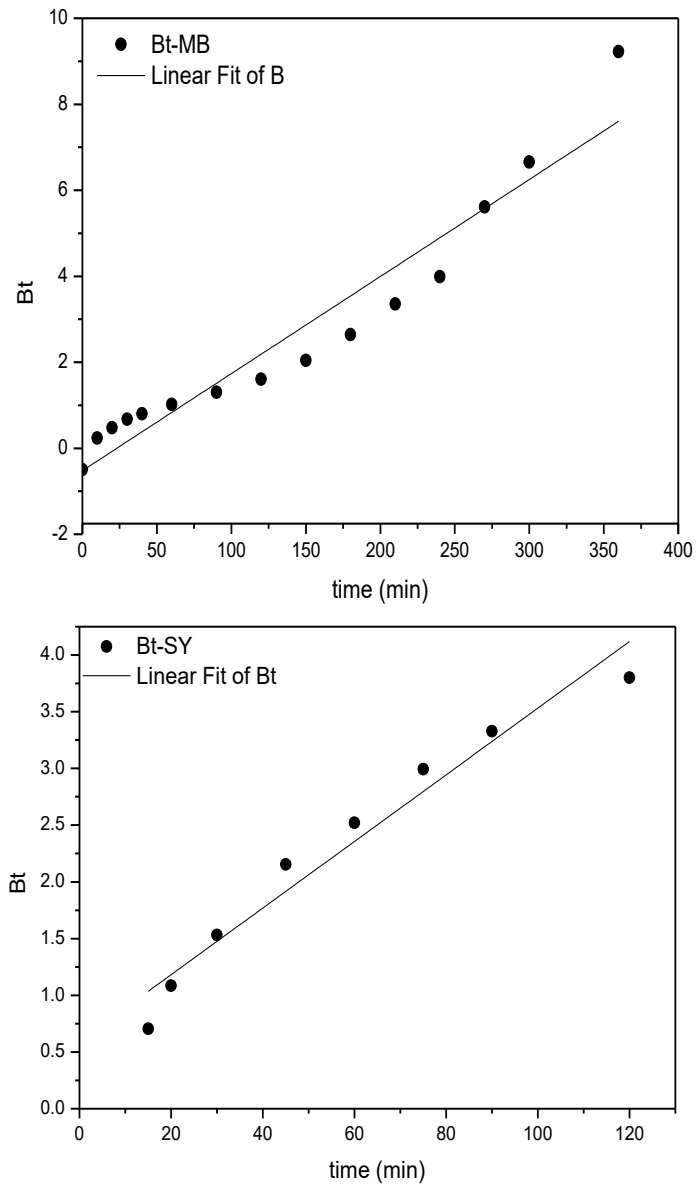


**Figure S13.** Kinetics of MB and SY adsorption by Hs-Cs-HAp





**Figure S14.** Pseudo-1st order and Pseudo-2<sup>nd</sup> order plots of MB-Hs-Cs-HAp and SY-Hs-Cs-HAp kinetic data.



**Figure S15.** Boyd plot of MB-Hs-Cs-HAp and SY-Hs-Cs-HAp kinetics data.