Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Production of chiral alcohols from racemic mixtures by integrated heterogeneous chemoenzymatic catalysis in fixed bed continuous operation

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Table S1. Elemental analysis of the support

Material	N%	H%	C%
ITQ-2	-	0.92	0.31
N-ITQ2	2.5	2.21	9.96

Table S2. Surface area of ITQ-2 zeolite, surface modified NITQ-2 and ADH@NITQ-2 catalyst.

Material	BET (m^2/g)	External surface area (m^2/g)
ITQ-2	756	592
NITQ-2	387	347
ADH@NITQ-2	219	96

Table S3. Evaluation of the contact time in flow reactor for the reduction of 2-octanone to (S)-2-octanol.

mmol/L	CT (h)	(%) Conversion (Selectivity)
30	4.0	97(100)
60	2.0	96(100)
94	1.3	90(100)
114	1.1	85(100)
160	0.8	54(100)

Conditions: ADH(S)@NITQ-2 (208.6 mg), NAD^+, (molar ratio substrate/cofactor = 10), in 10 mL of solvent (Isopropanol/phosphate buffer solution pH 7 100 mM (50/50 v/v), at 25 °C, flow 0.55 mL/h.

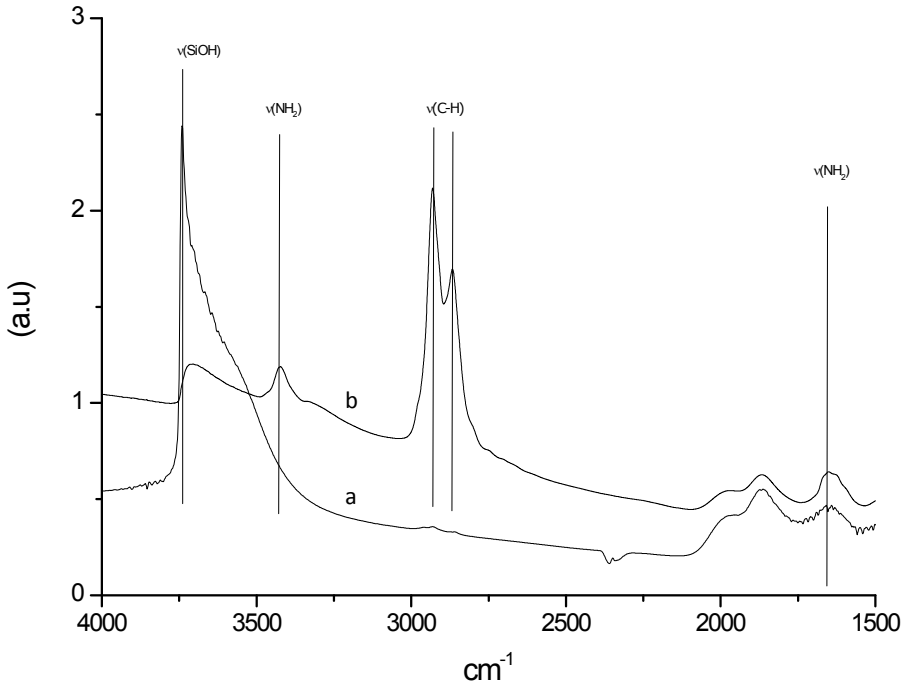

Figure S1. FTIR spectra of ITQ-2 pure silica (a); NITQ-2 (b)

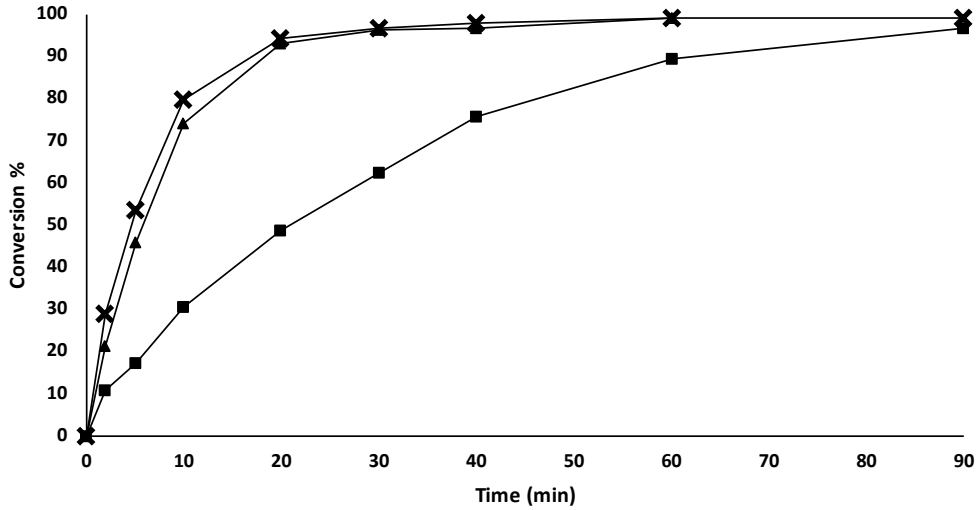

Figure S2. Catalytic activity of ADH(S)@NITQ-2 with different loadings in the conversion of 2-octanone into (S)-2-octanol. (✖) ADH8.6mg@NITQ-2, (▲) ADH7.5mg@NITQ-2, (■) ADH2.5mg@NITQ-2. Reaction conditions: 2-octanone, 0.3 mmol (30 mM), NAD^+, 0.03 mmol (molar ratio substrate/cofactor = 10), in 10 mL of solvent (Isopropanol/phosphate buffer solution pH 7 100 mM (50/50 v/v).

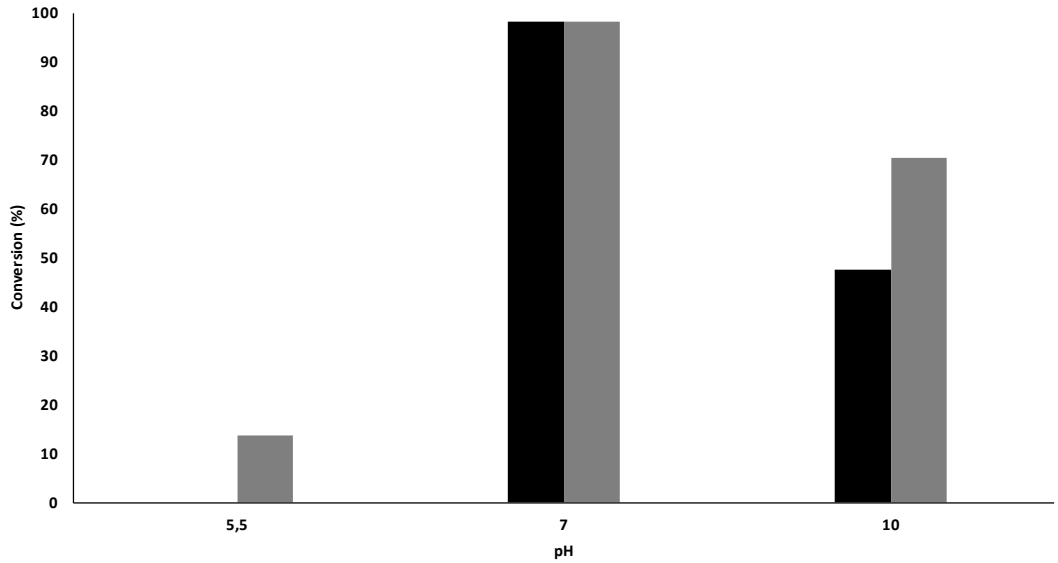

Figure S3. Effect of pH on the activity of ADH in the reduction of 2-octanone into (S)-2-octanol. (■) ADH(S) free, (■) ADH(S)@NITQ-2. Reaction conditions: ADH(S) (8.6 mg) or ADH(S)@NITQ-2 (208.6 mg), 2-octanone, 0.3 mmol (30 mM), NAD^+, 0.03 mmol (molar ratio substrate/cofactor = 10), in 10 mL of solvent (Isopropanol/phosphate buffer solution of pH 5.5, 7 and 10 (50/50 v/v), 1 h, at 25 °C.

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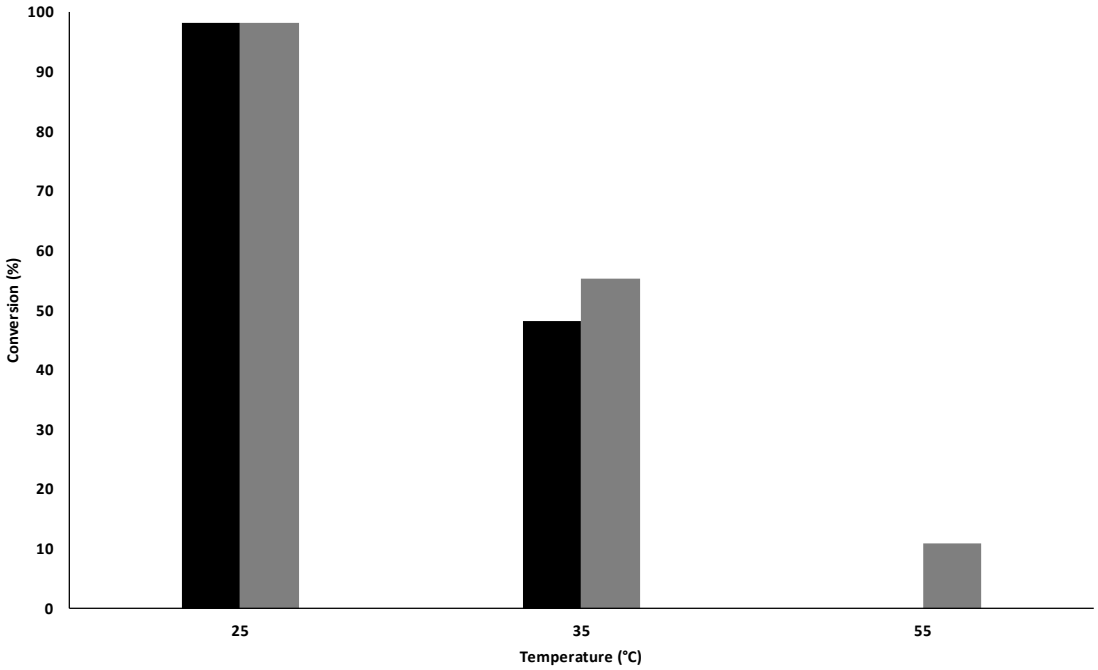

Figure S4. Thermal stability of the immobilized or free enzyme ADH(S). (■) ADH(S) free y (■) ADH(S)@NITQ-2. Reaction conditions: ADH(S) (8.6 mg) or ADH(S)@NITQ-2 (208.6 mg), 2-octanone, 0.3 mmol (30 mM), NAD^+, 0.03 mmol (molar ratio substrate/cofactor = 10), in 10 mL of solvent (Isopropanol/phosphate buffer solution pH 7 (50/50 v/v), 1 h, at 25 °C.

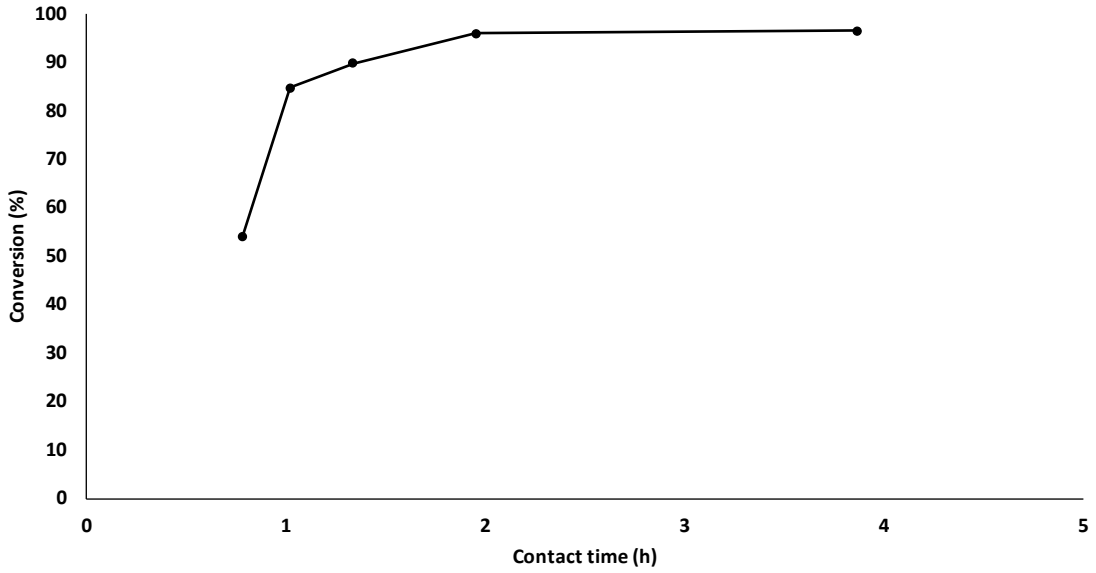

Figure S5. Evaluation of the contact time in flow reactor for the reduction of 2-octanone to (S)-2-octanol. Reaction conditions: ADH(S)@NITQ-2 (208.6 mg), (molar ratio substrate/cofactor = 10), 10 mL of solvent (Isopropanol/phosphate buffer solution pH 7 (50/50 v/v), flow 0.55 mL/h 25 °C.

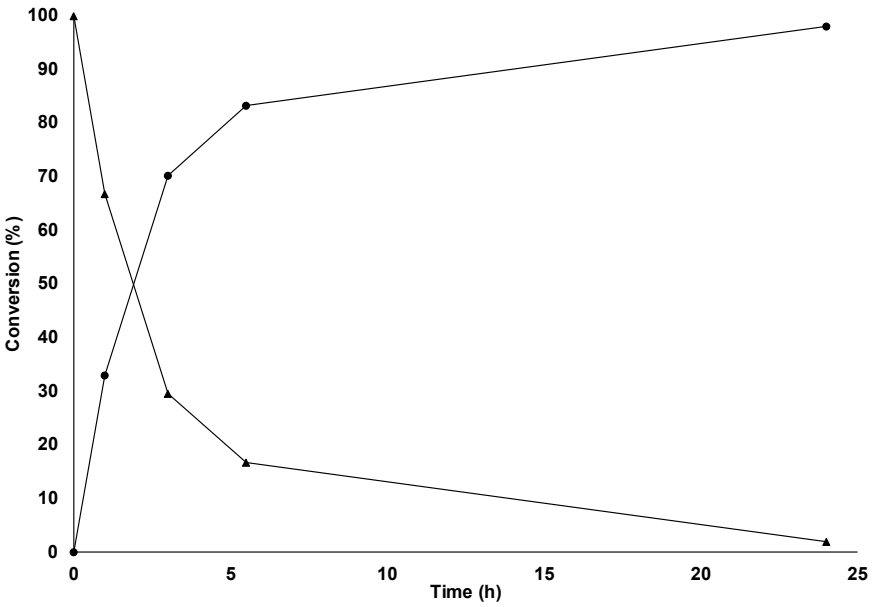

Figure S6. Oppenauer oxidation of rac-2-octanol using Zr-Beta zeolite.(▲) 2-octanol, (●) 2-octanone. Conditions: Zr-Beta (32 mg), 2-octanol (0.4 mmol), acetone (1.5 mL, 20.4 mmol), at 50 ºC.

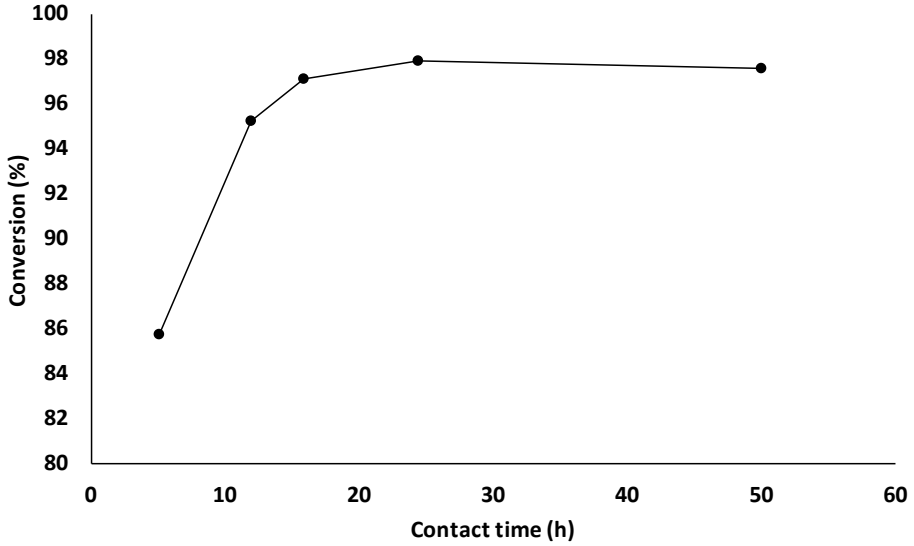

Figure S7. Evaluation of contact time in a continuos oxidation reactor. Reaction conditions: Zr-Beta (304 mg), acetone (10 mL, 136 mmol), flow 0.5 mL/h at 50 ^{o}C.

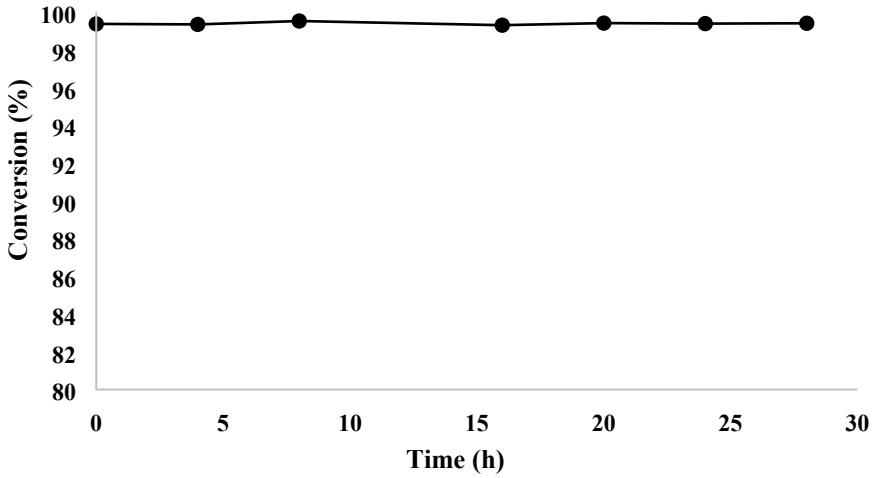

Figure S8. Evaluation of oxidation-reduction of rac-2-dodecanol in continuos reactor. Reaction conditions: First step: Zr-Beta (301 mg), acetone (10 mL, 136 mmol), 2-dodecanol 126 mmol/L, flow 0.5 mL/h at 50 ^{o}C. Second step: ADH(S)@NITQ-2 (208.6 mg), 2-dodecanone (30 mmol/L), NAD^{+} (3 mmol/L), solvent (Isopropanol/phosphate buffer solution pH 7 (50/50 v/v), flow 0.55 mL/h, 25 °C.

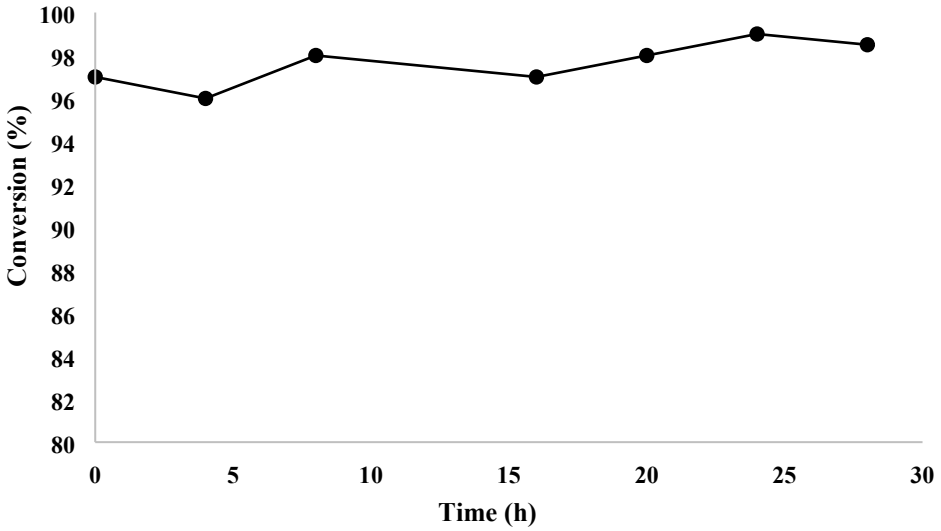

Figure S9. Evaluation of oxidation-reduction of rac-1-cyclohexylethanol in continuos reactor. Reaction conditions: First step: Zr-Beta (610 mg), acetone (10 mL, 136 mmol), rac-1-cyclohexylethanol 123 mmol/L, flow 0.2 mL/h at 50 ^{o}C. Second step: ADH(S)@NITQ-2 (208.6 mg), rac-1-cyclohexylethanone (30 mmol/L), NAD^{+} (3 mmol/L), solvent (Isopropanol/phosphate buffer solution pH 7 (50/50 v/v), flow 0.55 mL/h, 25 °C

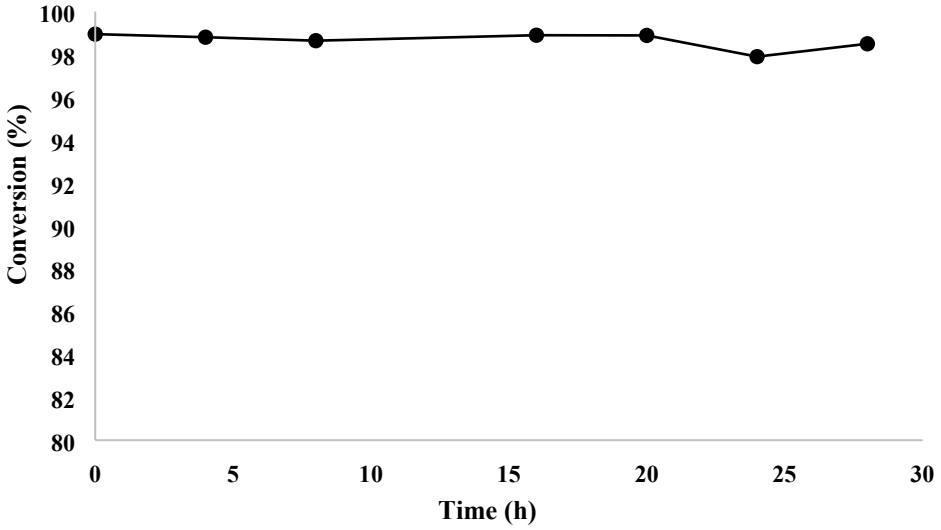

Figure S10. Evaluation of oxidation-reduction of rac-4-biphenylmethylcarbinol in continuos reactor. Reaction conditions: First step: Zr-Beta (610 mg), acetone (10 mL, 136 mmol), rac-4-biphenylmethylcarbinol 80 mmol/L, flow 0.2 mL/h at 50 ^{o}C. Second step: ADH(S)@NITQ-2 (208.6 mg), 4-acethylbiphenyl (30 mmol/L), NAD^{+} (3 mmol/L), solvent (Isopropanol/phosphate buffer solution pH 7 (50/50 v/v), flow 0.55 mL/h, 25 °C.

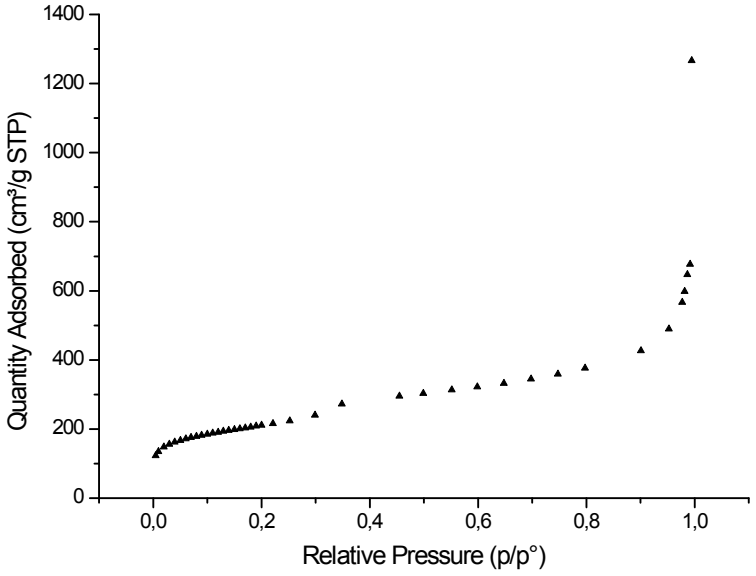

Figure S11. Nitrogen adsorption isotherm of ITQ-2 zeolite

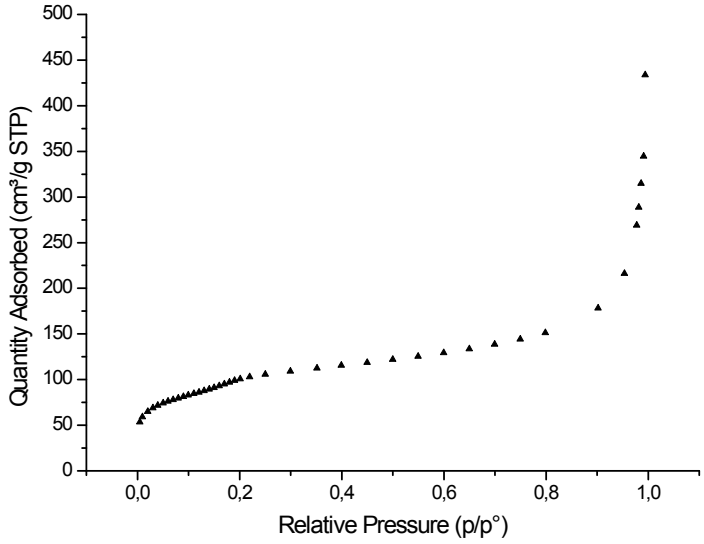

Figure S12. Nitrogen adsorption isotherm of NITQ-2 zeolite

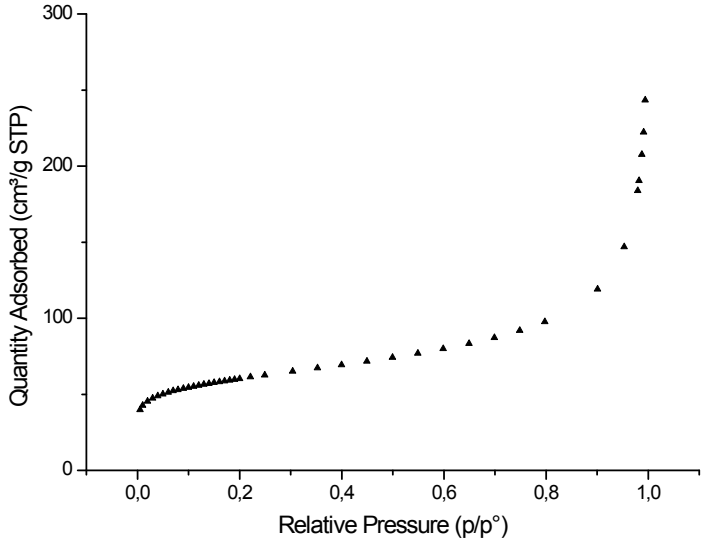

Figure S13. Nitrogen adsorption isotherm of ADH@NITQ-2 zeolite

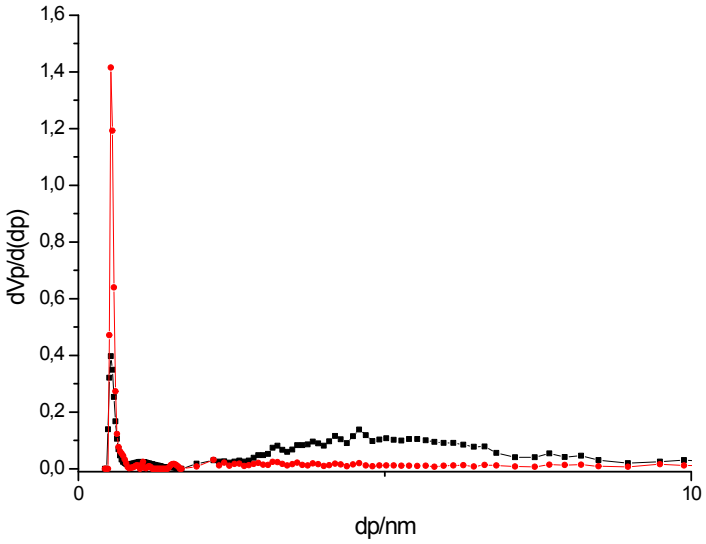

Figure S14. Pore volume distribution of ITQ2 zeolite (red) and ADH@NITQ2 (black)