Support Information

Nano scale manganese oxide within Faujasite zeolite as an efficient and biomimetic water oxidizing catalyst

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Material and methods

All reagents and solvents were purchased from commercial sources and were used without further purification. TEM and SEM were carried out with Philips CM120 and LEO 1430VP, respectively. The X-ray powder patterns were recorded with a Bruker, D8 ADVANCE (Germany) diffractometer (Cu-Kα radiation). Manganese atomic absorption spectroscopy (AAS) was performed on an Atomic Absorbtion Spectrometer Varian Spectr AA 110. Prior to analysis, the oxide (10.0 mg metal) were added to 1 mL of concentrated nitric acid and H_2O_2, left at room temperature for at least 1 h to ensure that the oxides were completely dissolved. The solutions were then diluted to 25.0 mL and analyzed by AAS.

Synthesis

First, $Mn(CH_3COO)_2.4H_2O$ in 50 mL water was introduced into faujasite zeolite at room temperature for 4 h. After washing, $KMnO_4$ in KOH solution (50 mL water, 0.1 M KOH) was added to the manganese ion-containing faujasite zeolite. After two hours, the solid was filtered, washed and dried at 60 ^{o}C.

Table 1S.

Sample	$Mn(CH_3COO)_2.4H_2O$ used in ion exchange (M)	$KMnO_4$ (M)	Mn content of zeolite (wt %)
1	0.0081	0.0064	0.65
2	0.016	0.012	1.14
3	0.024	0.019	1.47
4	0.032	0.025	1.68
5	0.04	0.032	1.98
6	0.081	0.036	2.34
7	0.163	0.046	2.47
8	0.244	0.054	2.52
9	0.326	0.064	2.87
10	0.408	0.077	2.96
11	0.571	0.09	3.46
12	0.816	0.12	3.73
13	*	*	5.64

**Best catalyst (%*5.64*):*

First, $Mn(CH_3COO)_2.4H_2O$ (0.2 M, 50 mL) was introduced into faujasite zeolite at room temperature for 24 h. Then zeolite was washed and, again, $Mn(CH_3COO)_2.4H_2O$ (0.2 M, 50 mL) was added to zeolite at room temperature for 24 h. This procedure was repeated by $Mn(CH_3COO)_2.4H_2O$ (0.5 M, 50 mL) two times. After washing, $KMnO_4$ in KOH solution (7.0 gr, 50 mL water, 0.1 M KOH) was added to the manganese ion-containing faujasite zeolite. After two hours, the solid was filtered, washed and dried at 60 ^{o}C.

Water Oxidation

Oxygen evolution from aqueous solutions in the presence of $(NH_4)_2Ce(NO_3)_6$ (Ce(IV)) was measured using an HQ40d portable dissolved oxygen meter connected to an oxygen monitor with digital readout. The reactor was maintained at 25.0 ºC in a water bath. In a typical run, the instrument readout was calibrated against air-saturated distilled water stirred continually with a magnetic stirrer in the air-tight reactor. After ensuring a constant baseline reading, the water in the reactor was replaced with Ce(IV) solution. Without catalyst, Ce(IV) was stable in this condition and oxygen evolution was not observed. After deaeration of Ce(IV) solution with argon, manganese oxides as several small particles were added, and oxygen evolution was recorded with the oxygen meter under stirring (Fig. S1). The formation of oxygen was followed, and oxygen formation rates per manganese site were obtained from linear fits of the data.

Electronic Supplementary Material (ESI) for Dalton Transactions

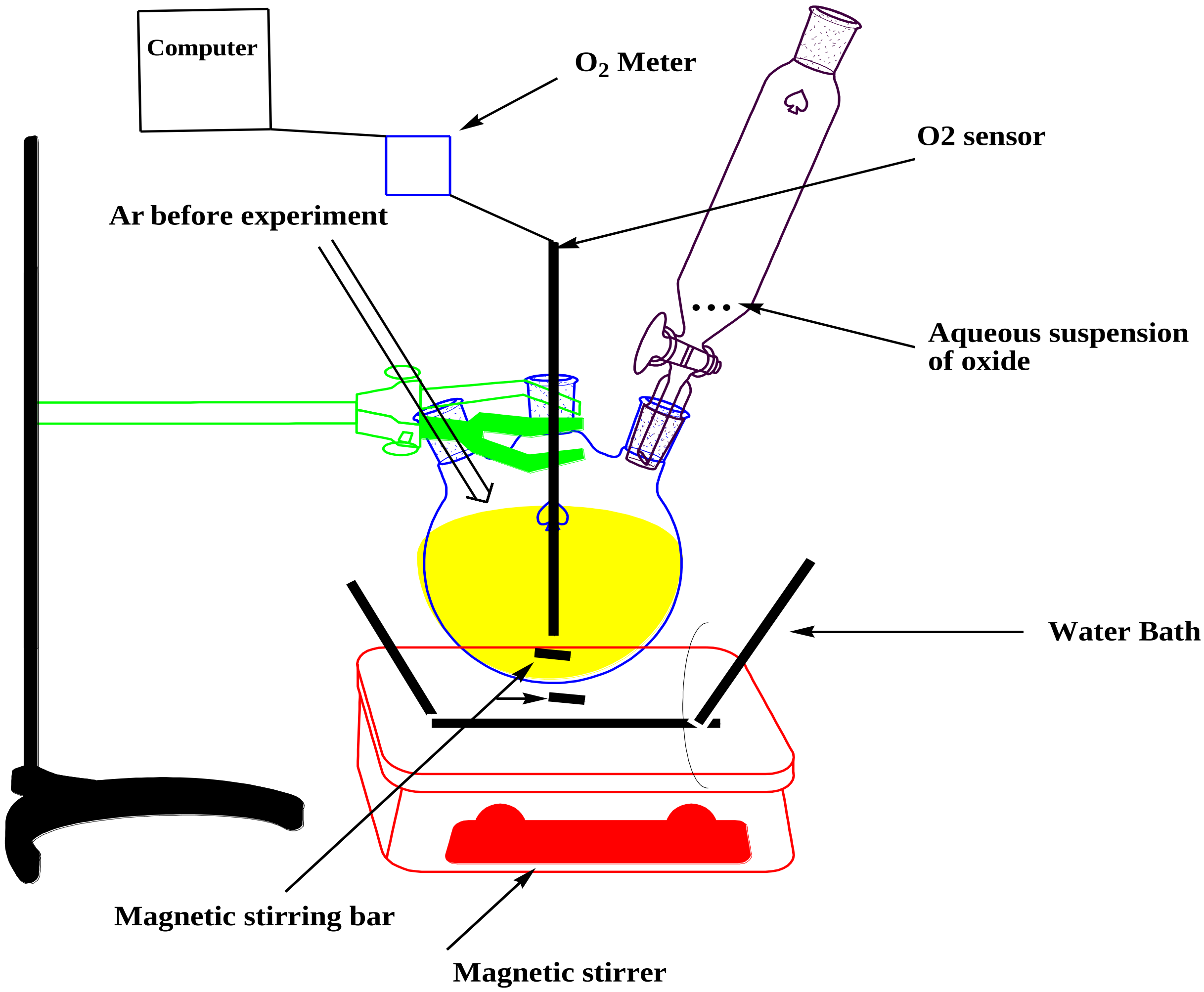


Fig. S1. The reactor set-up for oxygen evolution experiment from aqueous solution in the presence $(NH_4)_2Ce(NO_3)_6$ (Ce(IV)) and manganese oxide within Faujasite zeolite.

Electronic Supplementary Material (ESI) for Dalton Transactions

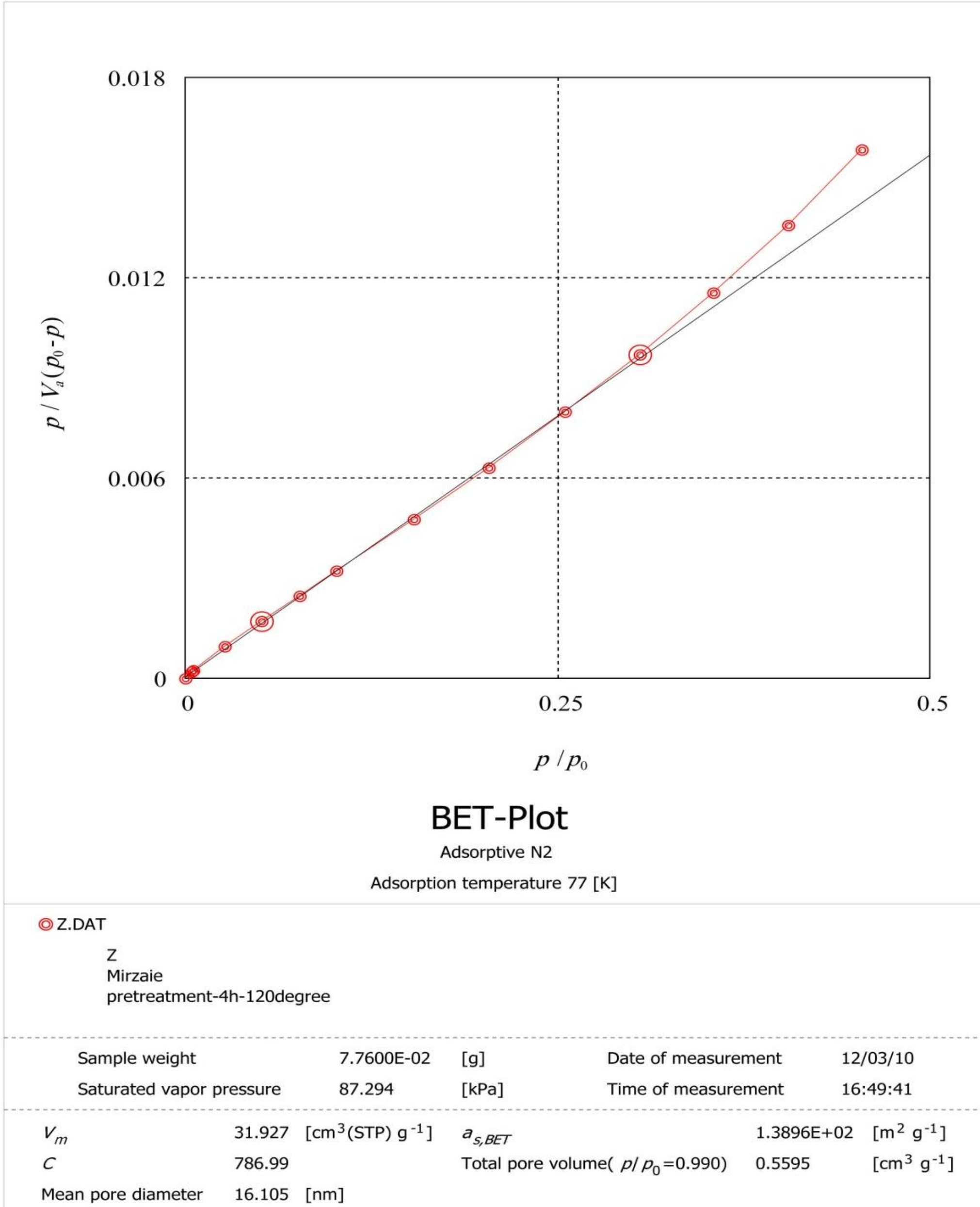
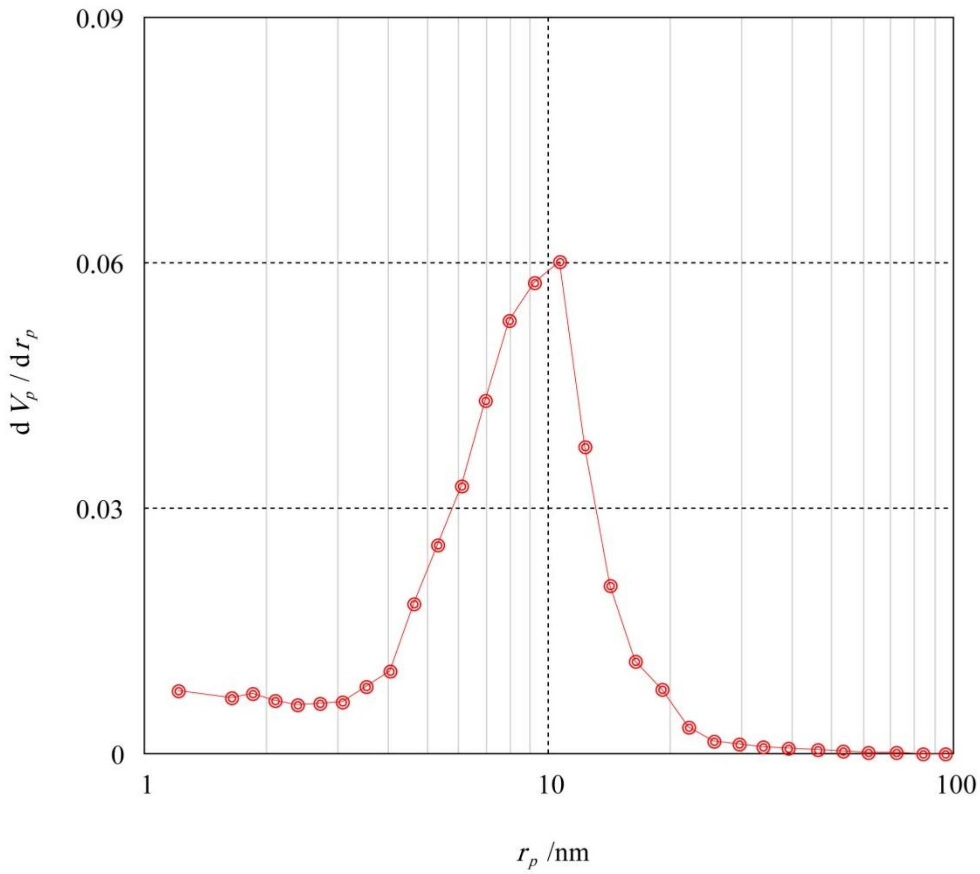


Fig. S2. BET diagram for Faujasite zeolite



BJH-Plot

Adsorption branch

Adsorptive N2

Adsorption temperature 77 [K]

Z.DAT

Z
Mirzaie
pretreatment-4h-120degree

Sample weight	7.7600E-02	[g]	Date of measurement	12/03/10	
Saturated vapor pressure	87.294	[kPa]	Time of measurement	16:49:41	

V_p	0.5475	[cm^3 g^{-1}]	$r_{p,peak}$(*Area*)	10.65	[nm]
a_p	129.25	[m^2 g^{-1}]			

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Fig. S3. BJH diagram for Faujasite zeolite

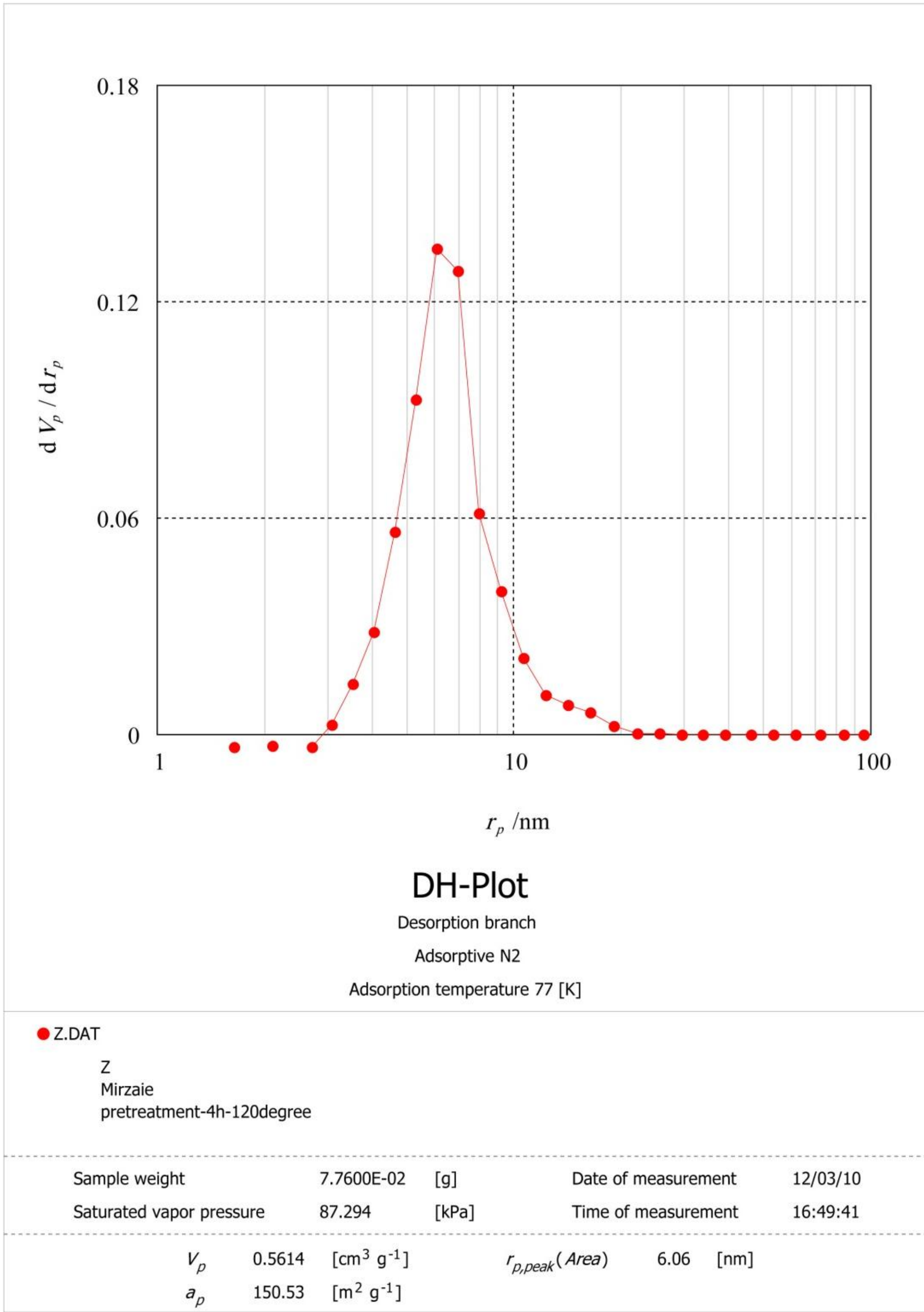


Fig. S4. DH diagram for Faujasite zeolite

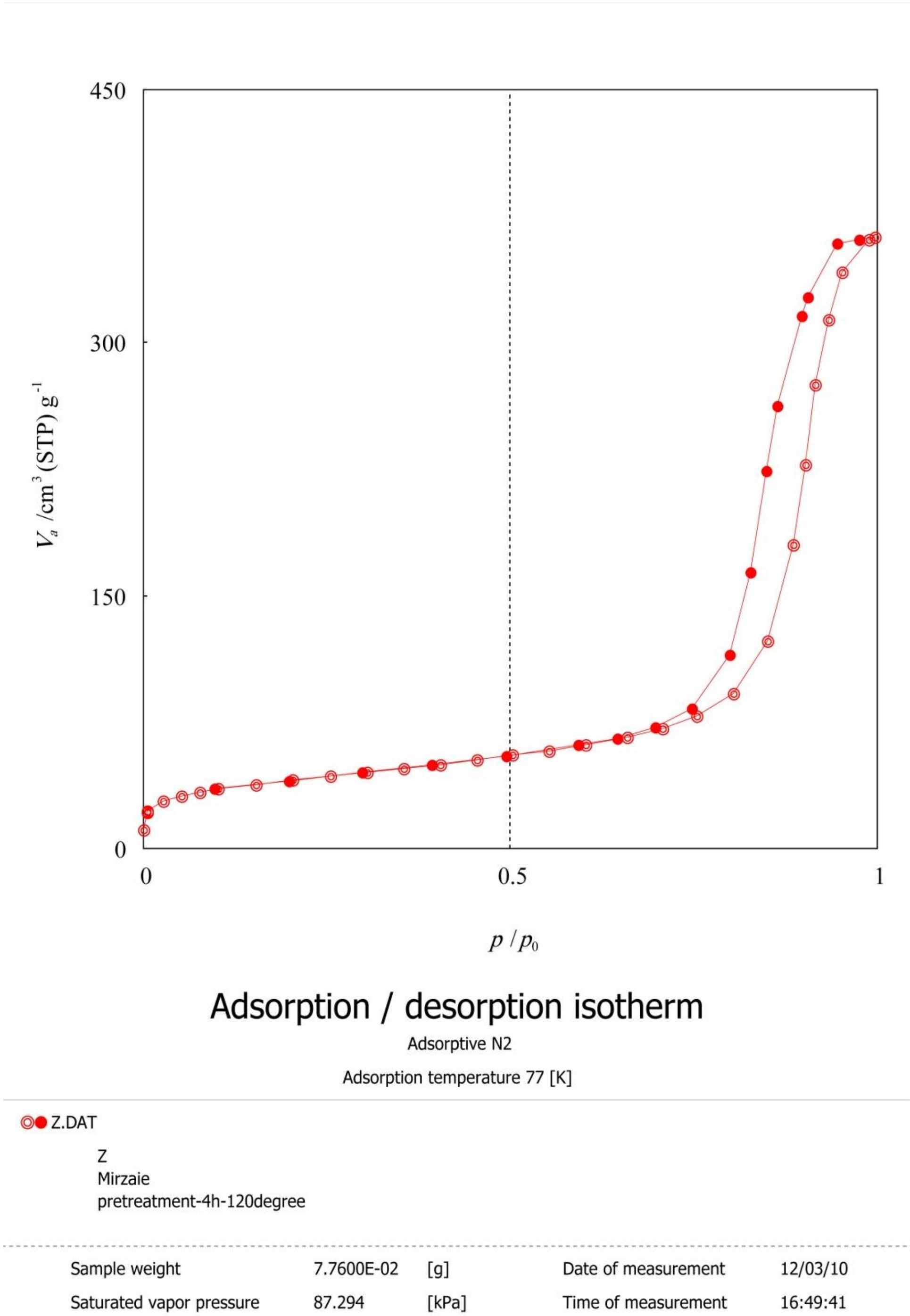
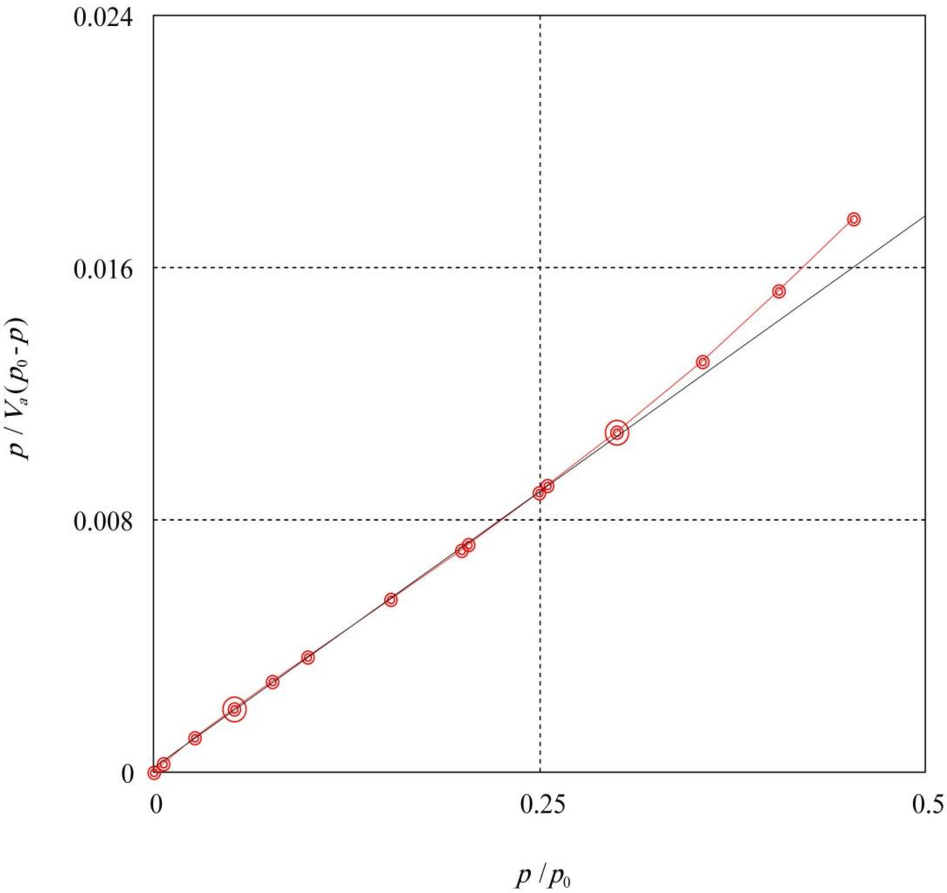


Fig. S5. Adsorption / Desorption Isotherm diagram for Faujasite Zeolite



BET-Plot

Adsorptive N2

Adsorption temperature 77 [K]

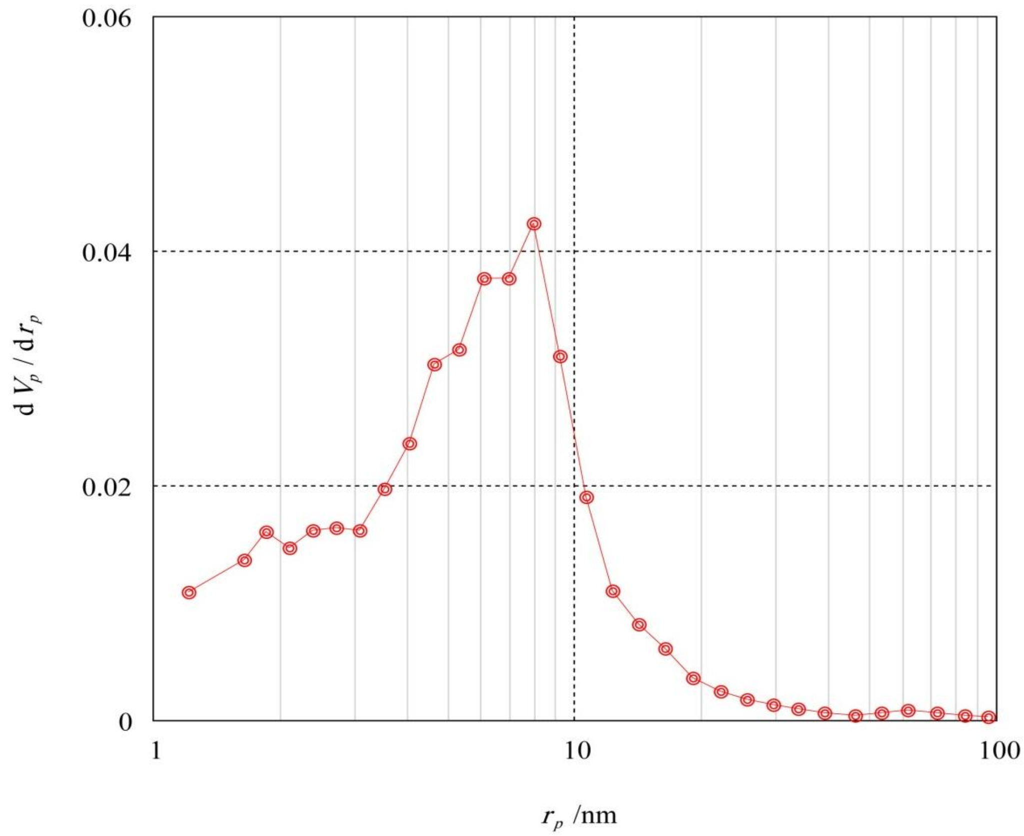
◎ Z5D.DAT

Z5D
Mirzaie
pretreatment-4h-120degree

Sample weight	4.8400E-02	[g]	Date of measurement	12/03/10
Saturated vapor pressure	87.567	[kPa]	Time of measurement	12:24:00

V_m	28.473	[cm^3(STP) g^{-1}]	$a_{s,BET}$	1.2393E+02	[m^2 g^{-1}]
C	224.70		Total pore volume(p/p_0=0.990)	0.4165	[cm^3 g^{-1}]
Mean pore diameter	13.444	[nm]			

Fig. S6. BET diagram for manganese oxide within Faujasite zeolite



BJH-Plot

Adsorption branch

Adsorptive N2

Adsorption temperature 77 [K]

Z5D.DAT

Z5D
Mirzaie
pretreatment-4h-120degree

Sample weight	4.8400E-02	[g]	Date of measurement	12/03/10
Saturated vapor pressure	87.567	[kPa]	Time of measurement	12:24:00

V_p	0.4096	$[cm^3\ g^{-1}]$	$r_{p,peak}$(*Area*)	7.99	[nm]
a_p	122.68	$[m^2\ g^{-1}]$			

Fig. S7. BJH diagram for manganese oxide within Faujasite zeolite

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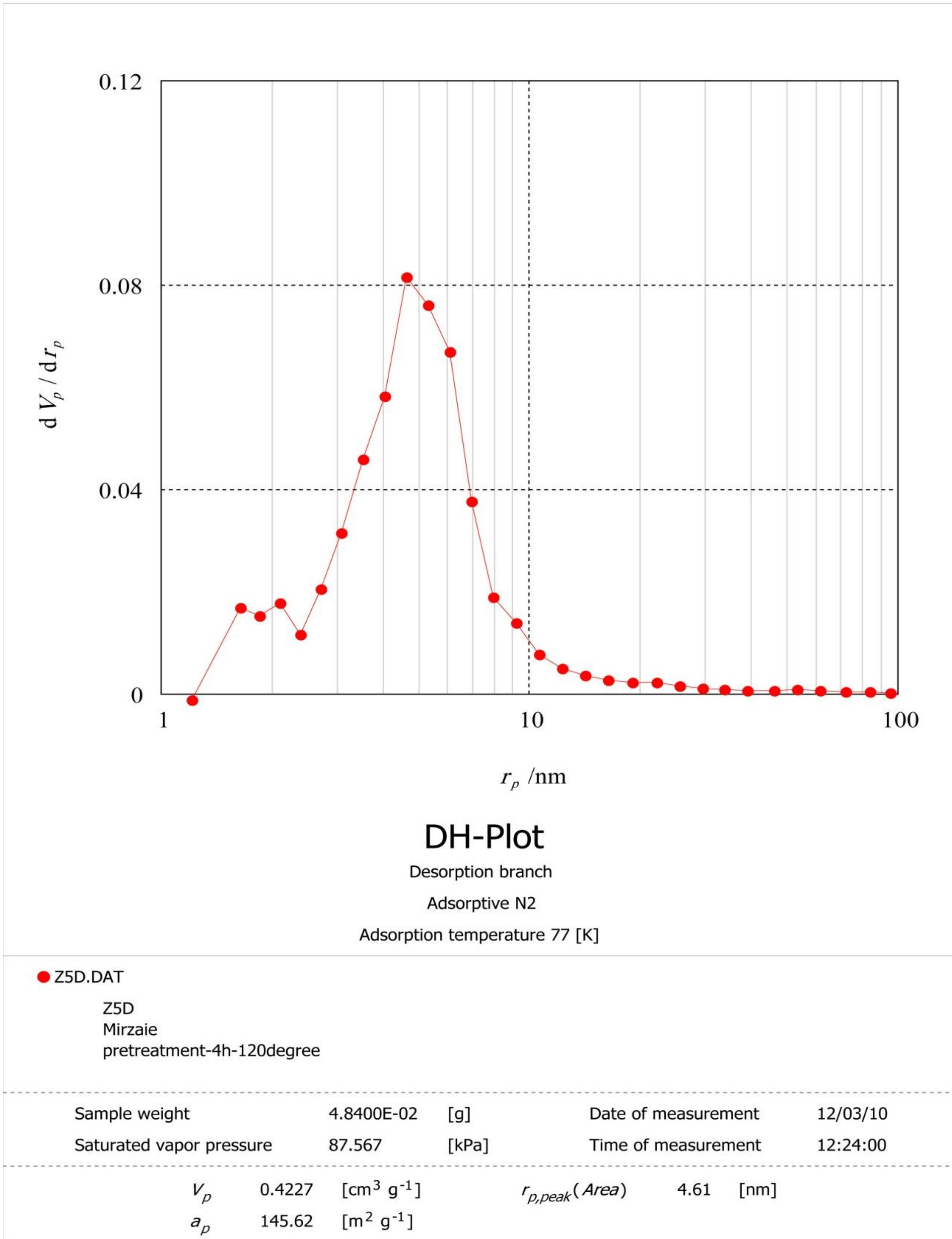


Fig. S8. DH diagram for manganese oxide within Faujasite zeolite

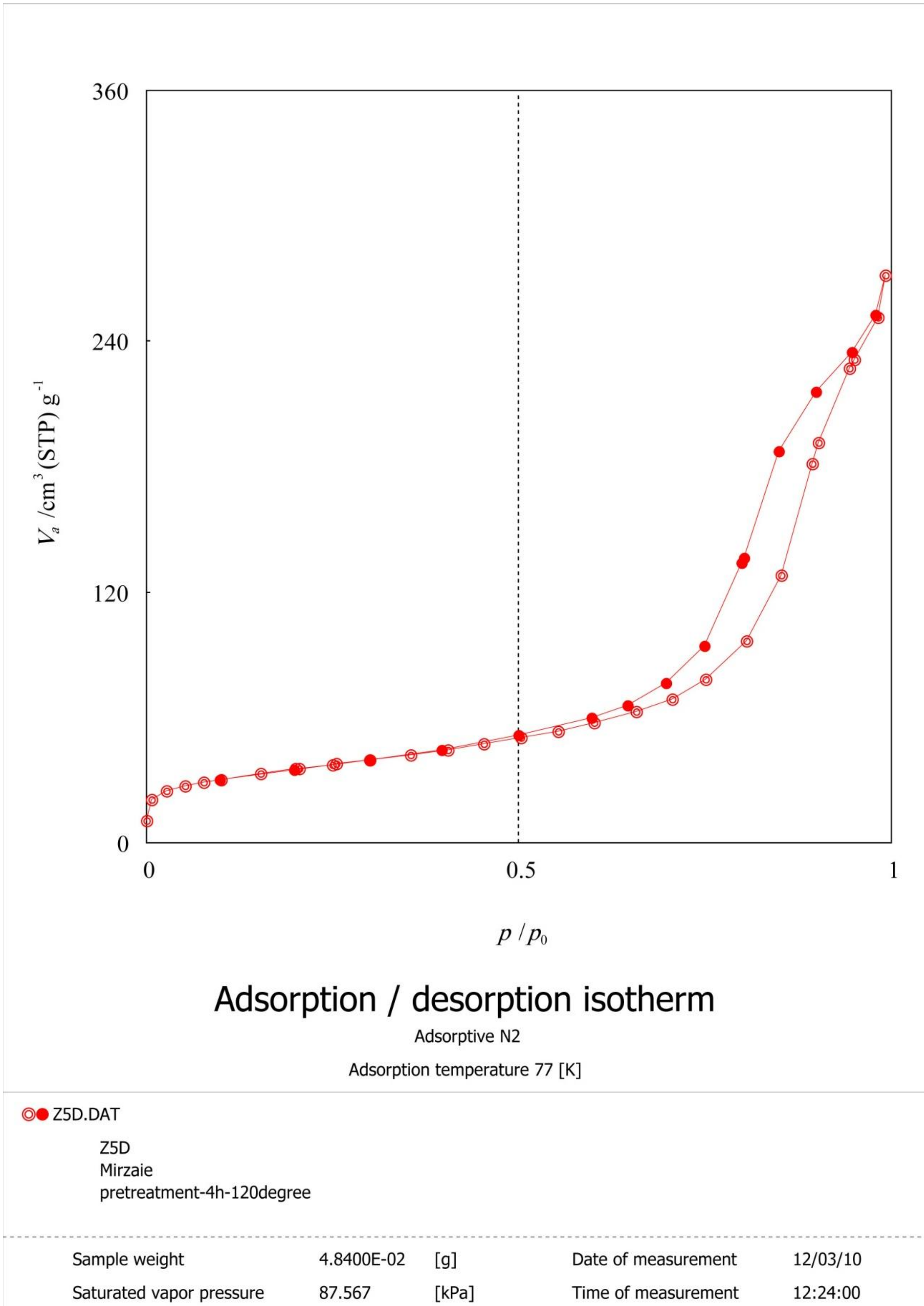
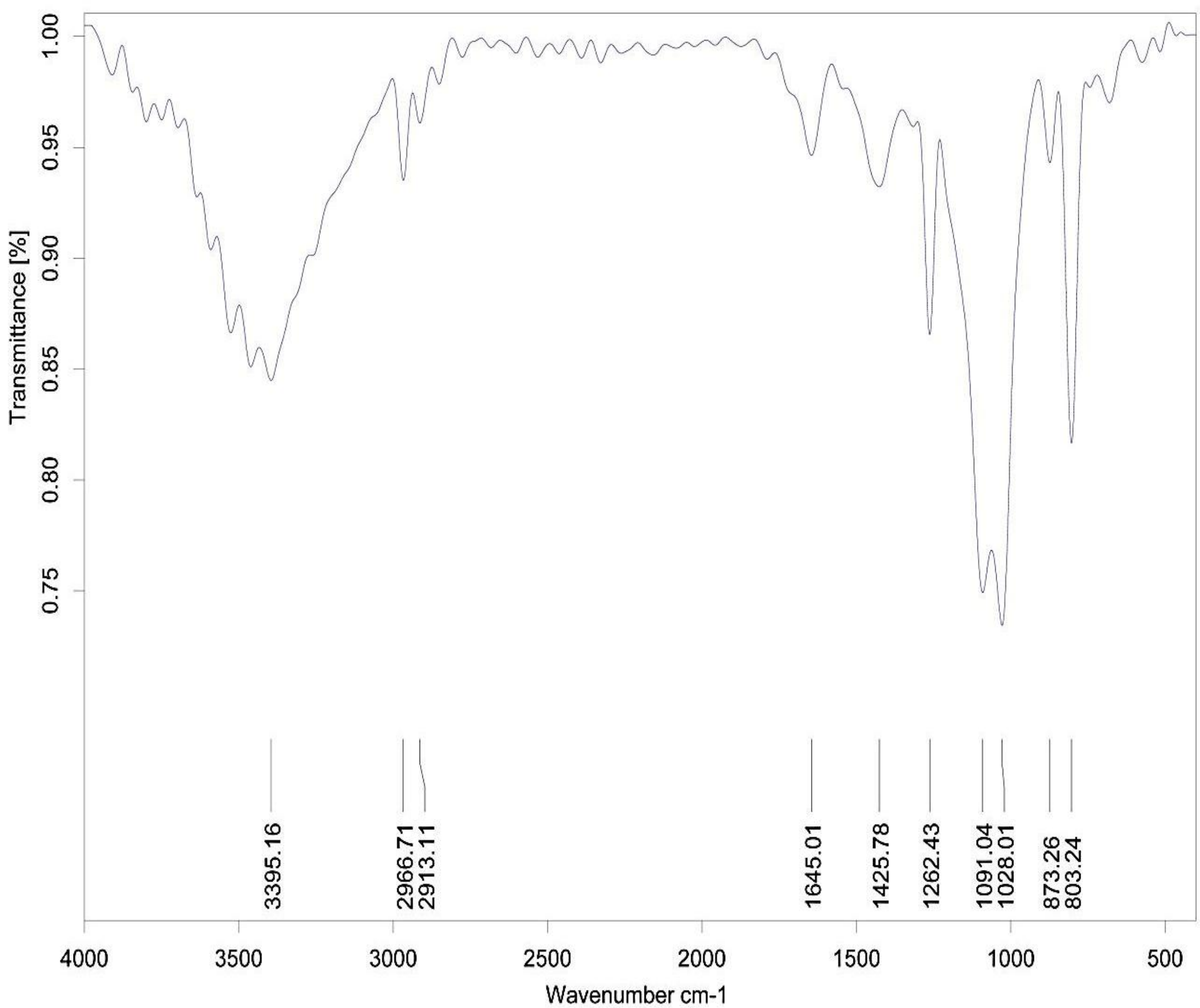


Fig. S9. Adsorption / Desorption Isotherm diagram for manganese oxide within Faujasite zeolite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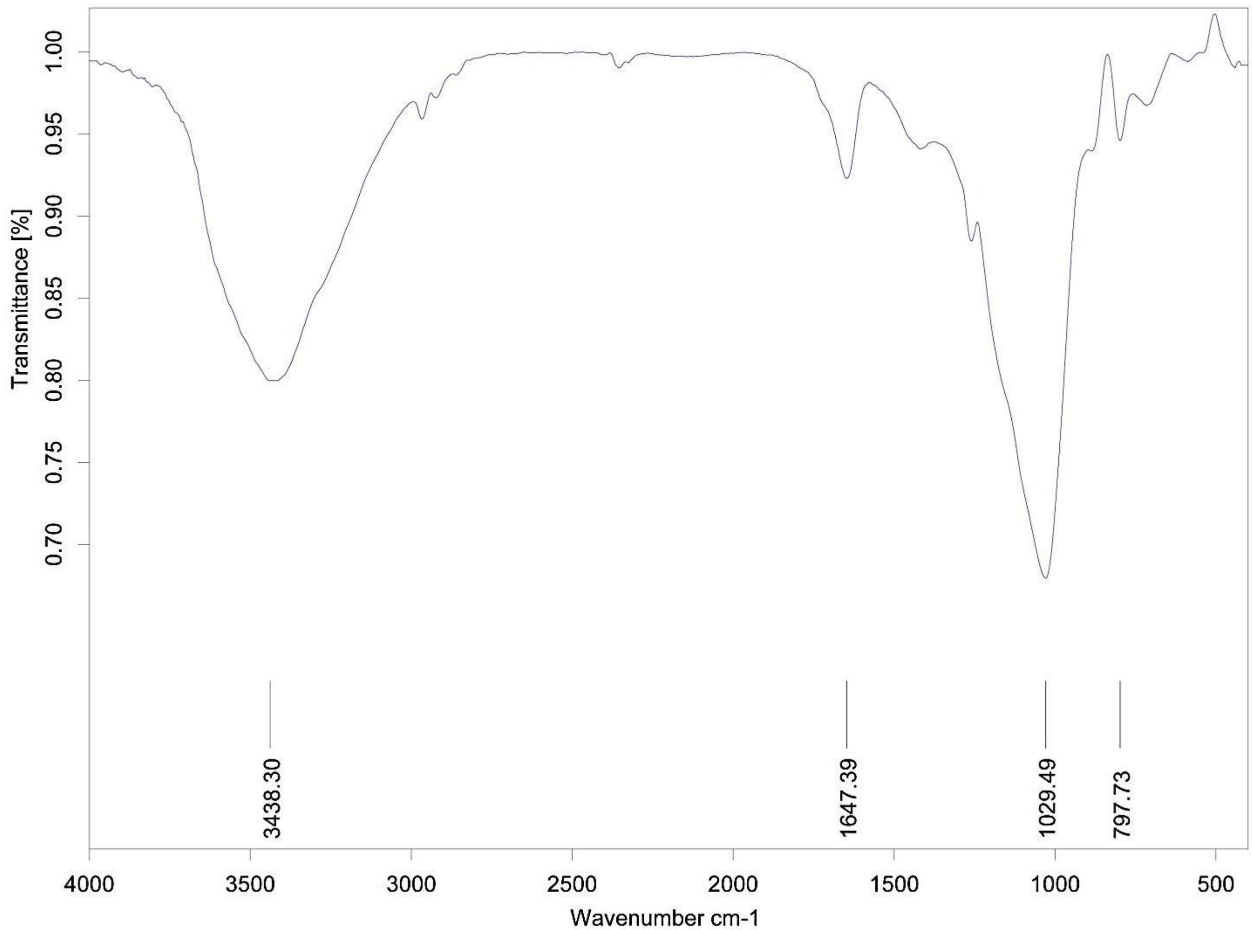
2000
1500
1000
500
Wavenumber cm-1

(a)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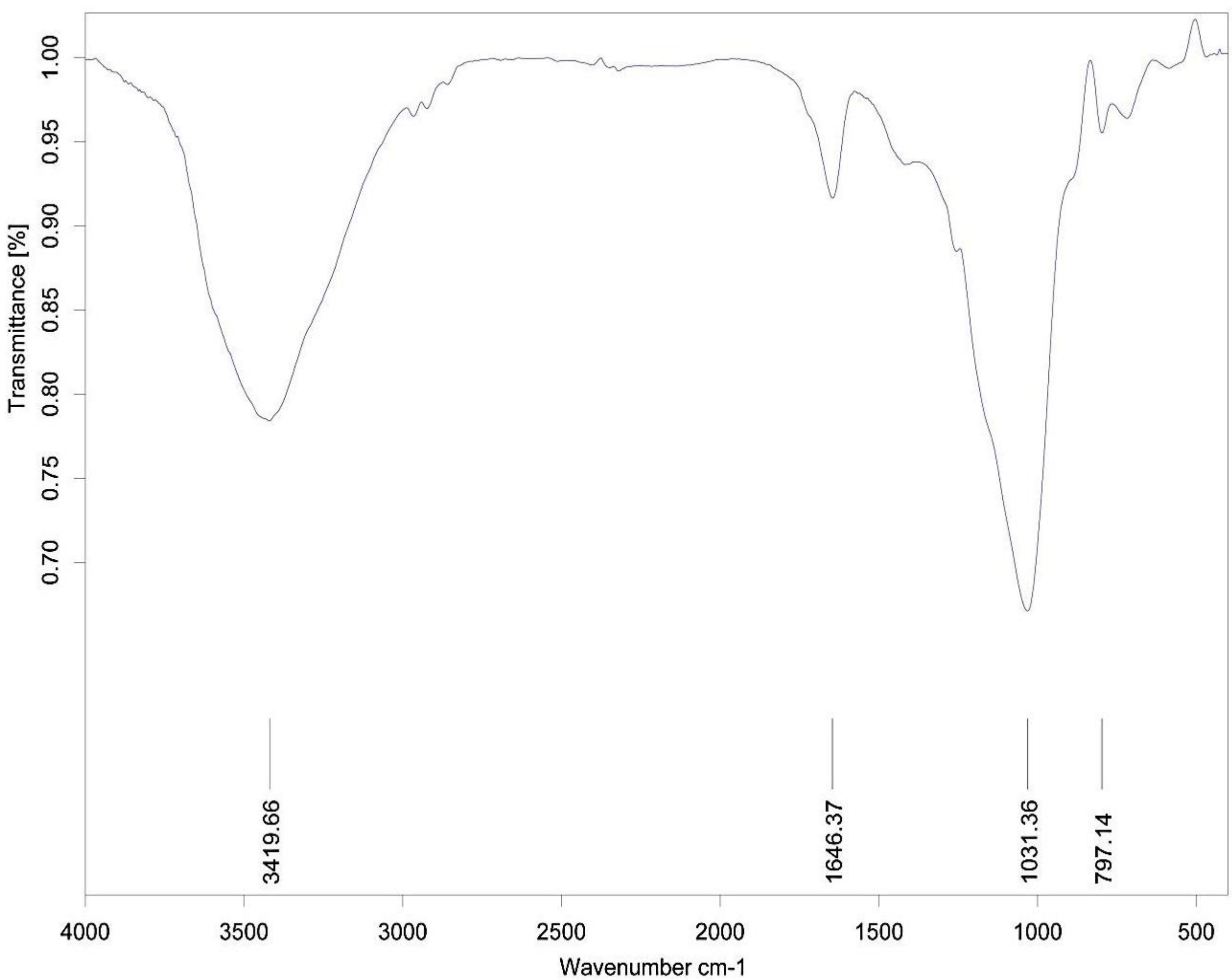
Wavenumber cm-1

(b)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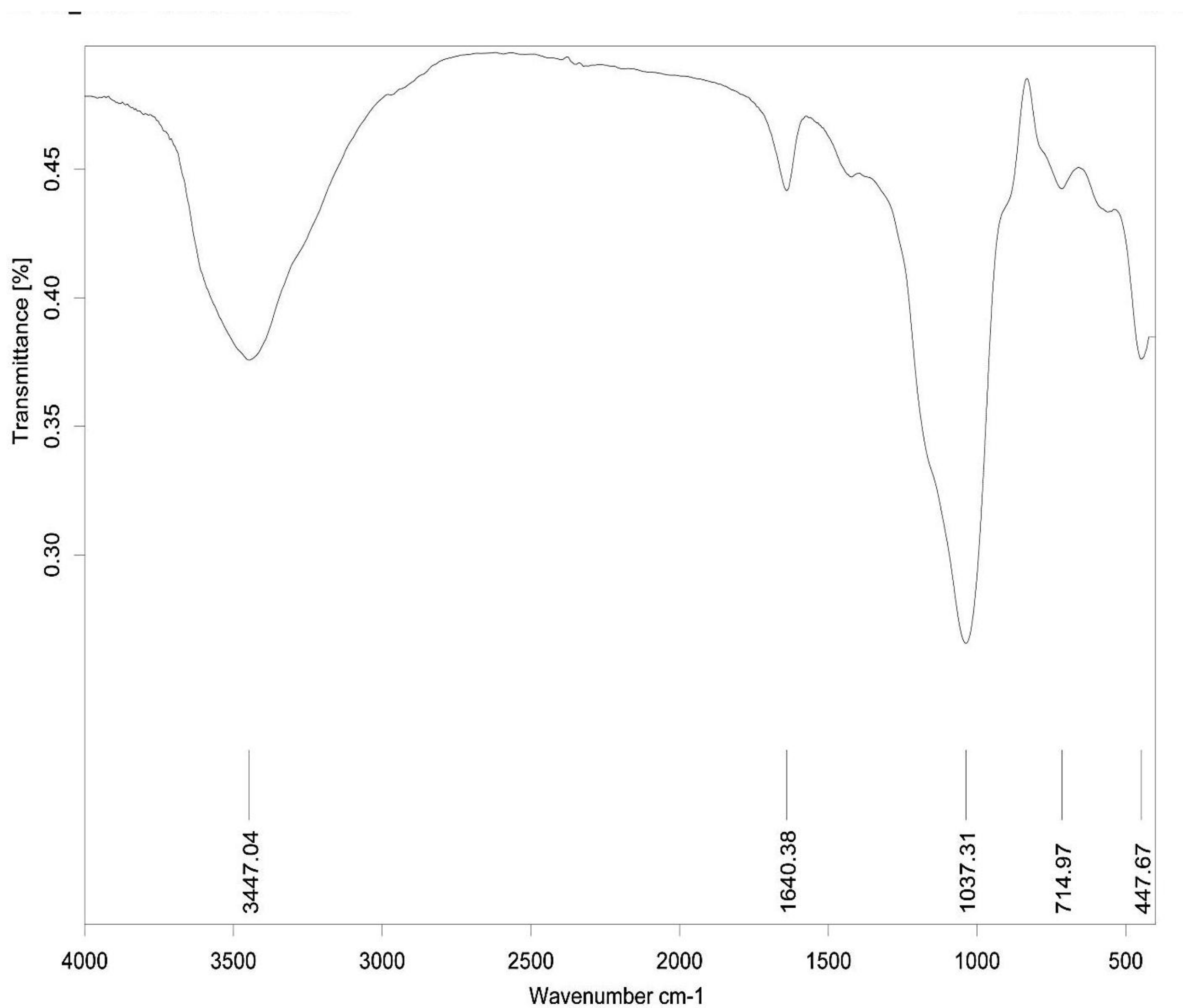
1500
1000
500
Wavenumber cm-1

(c)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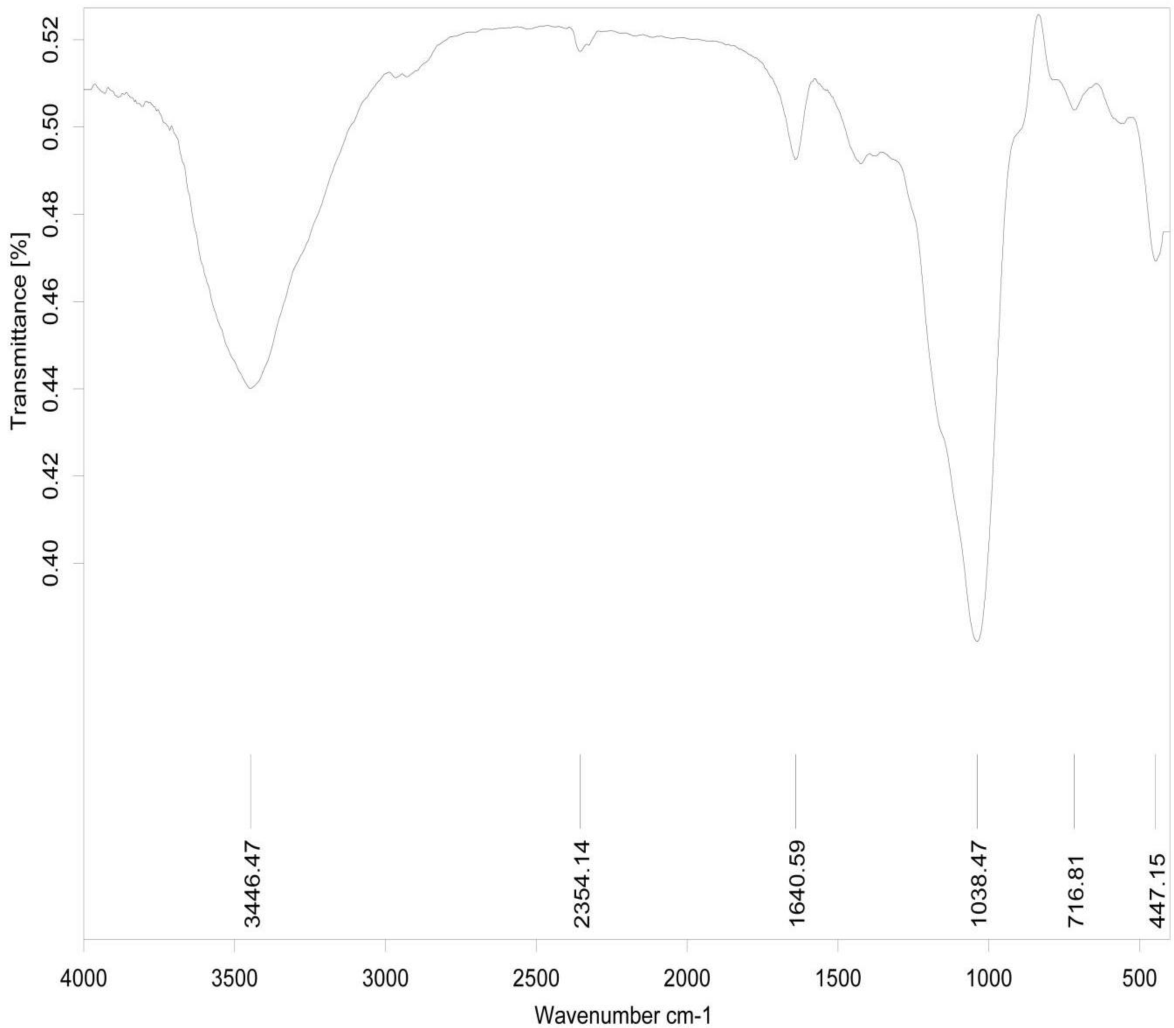
(d)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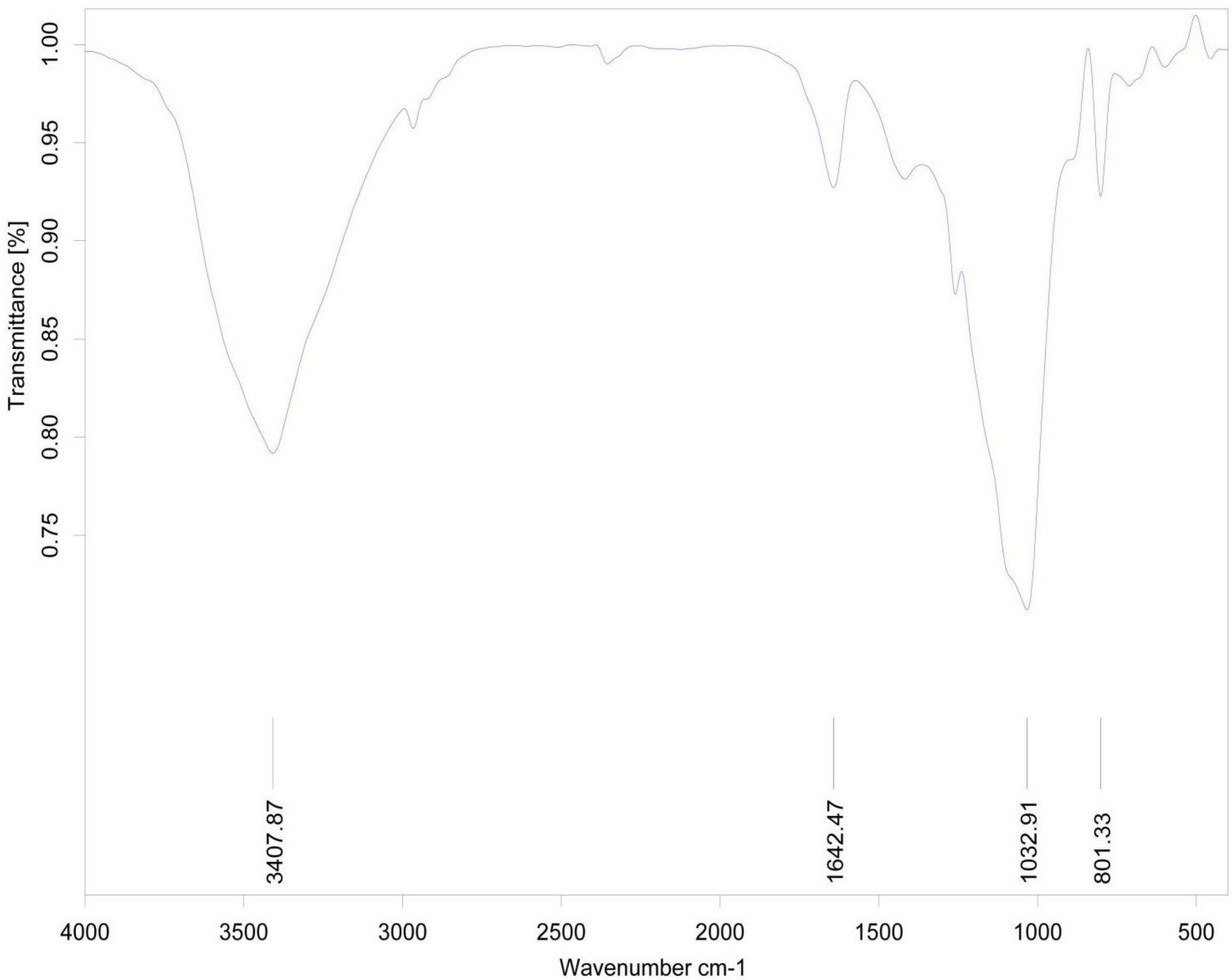
Wavenumber cm-1

(e)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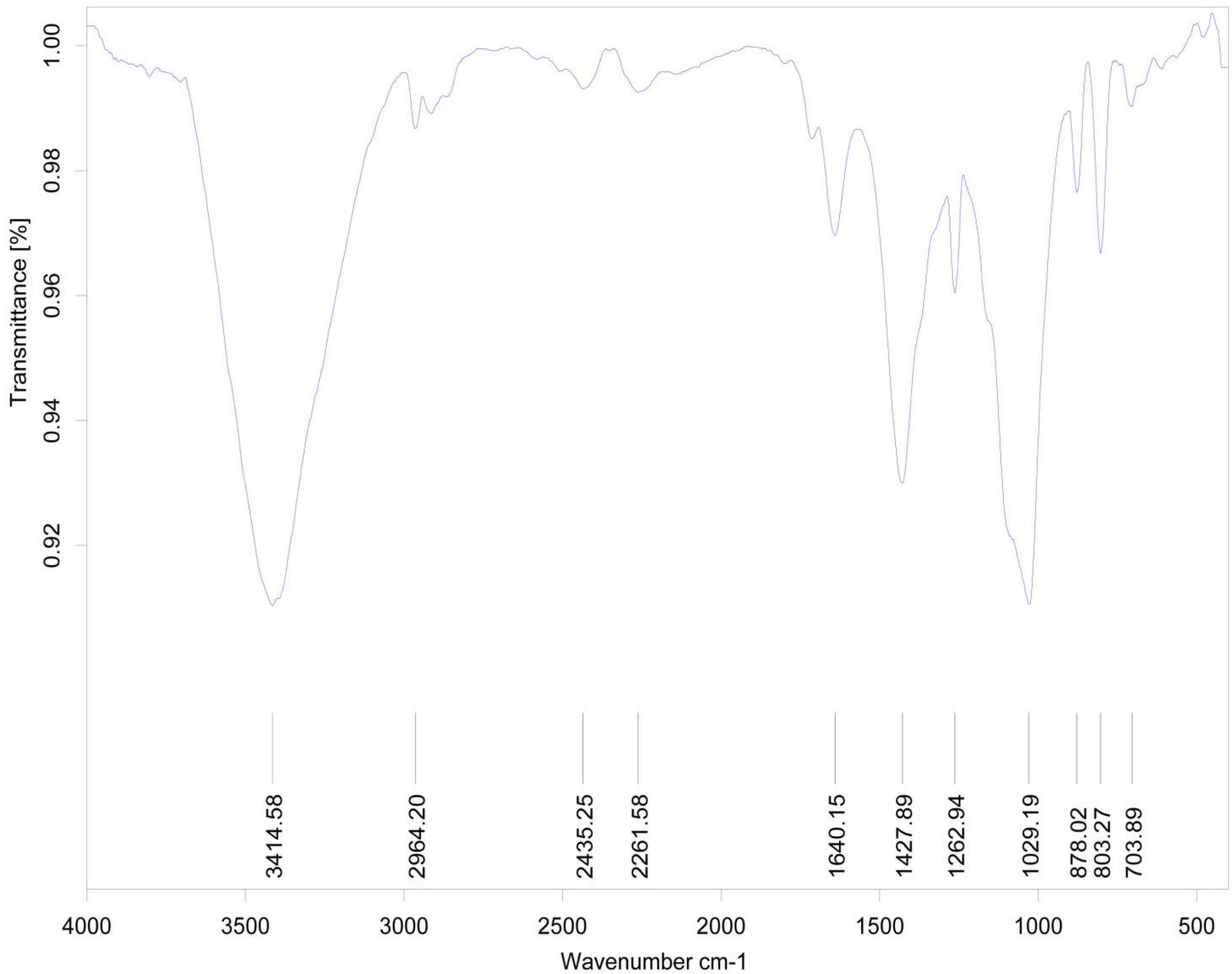
Wavenumber cm-1

(f)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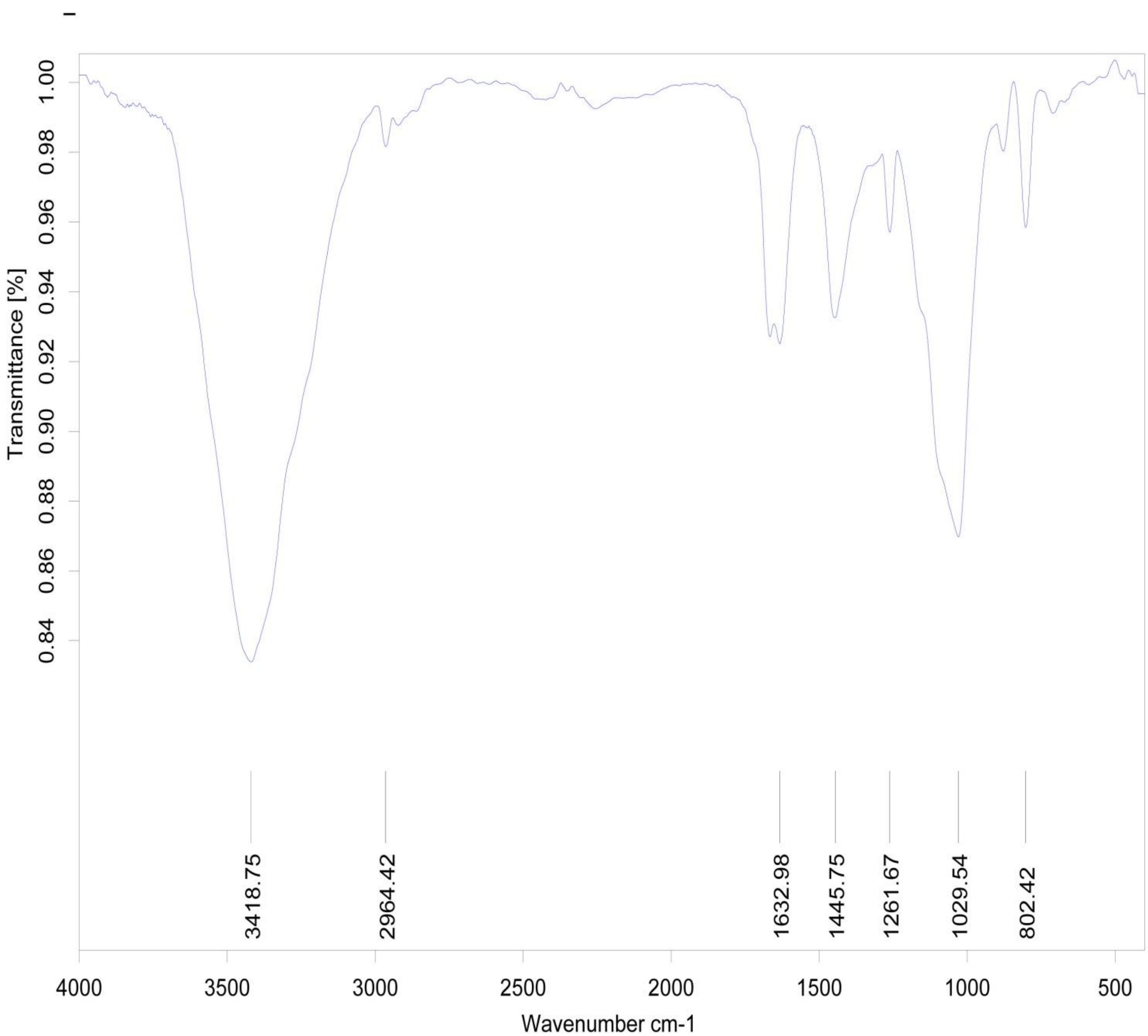
Wavenumber cm-1

(g)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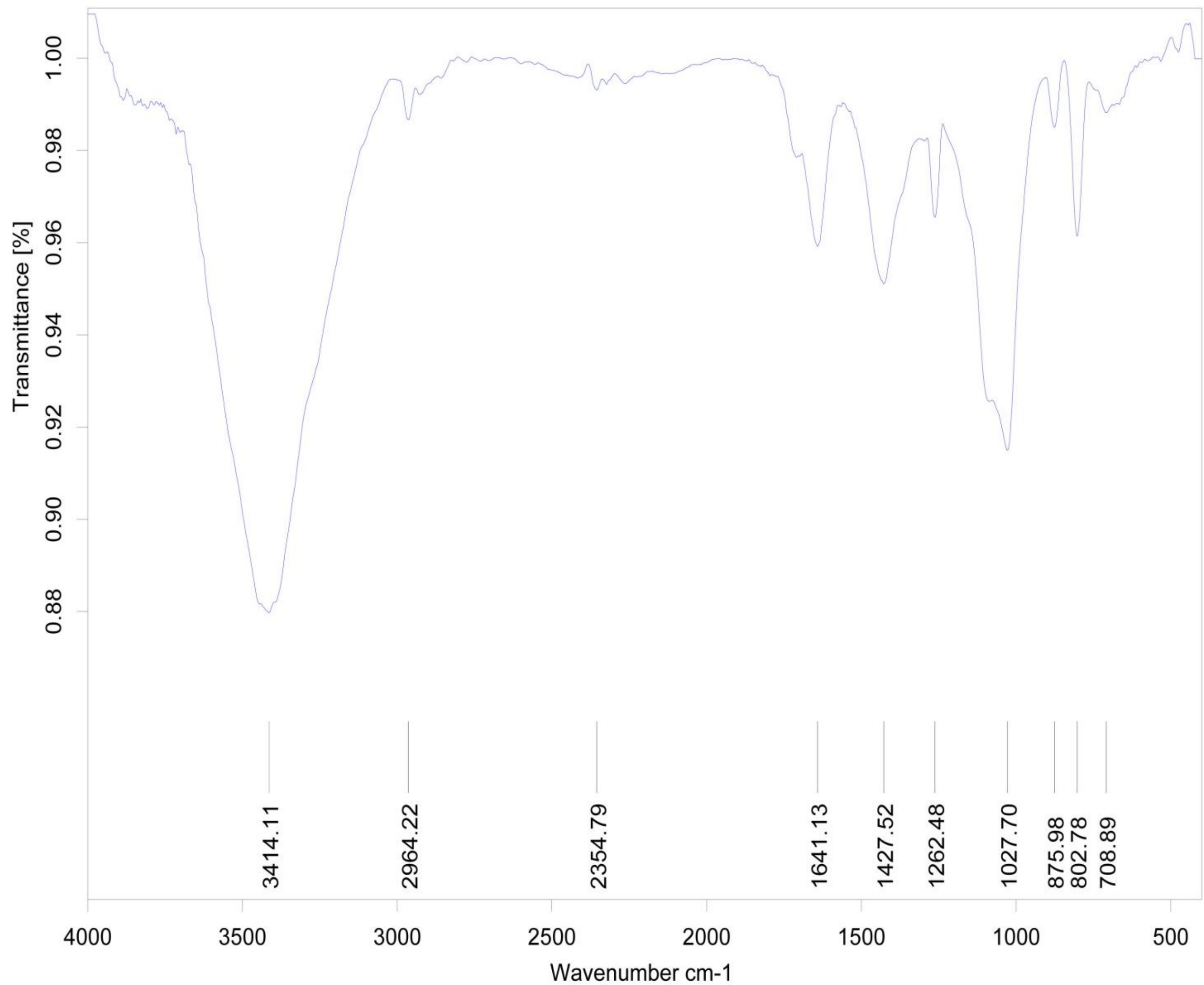
Wavenumber cm-1

(h)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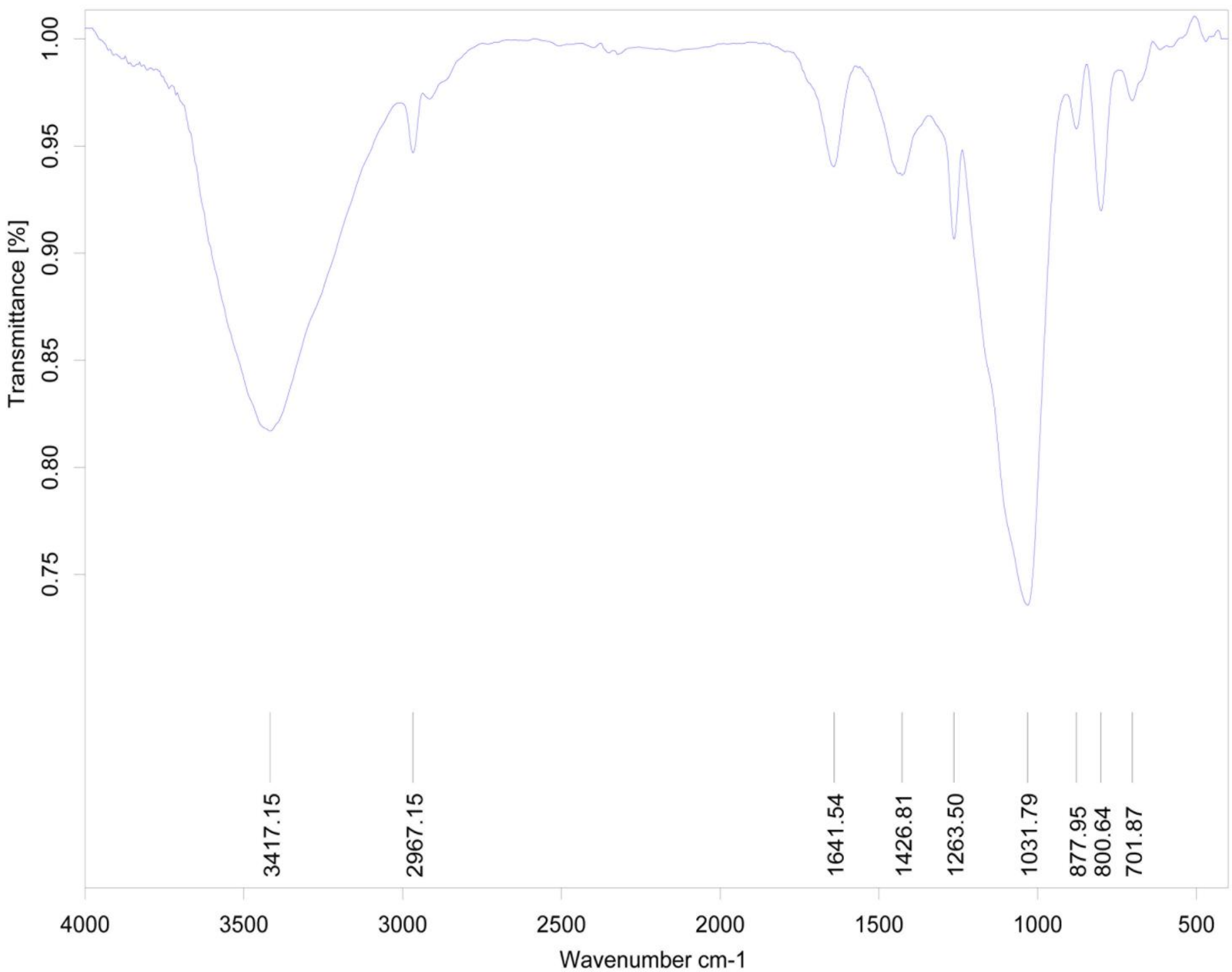
2000
1500
1000
500
Wavenumber cm-1

(i)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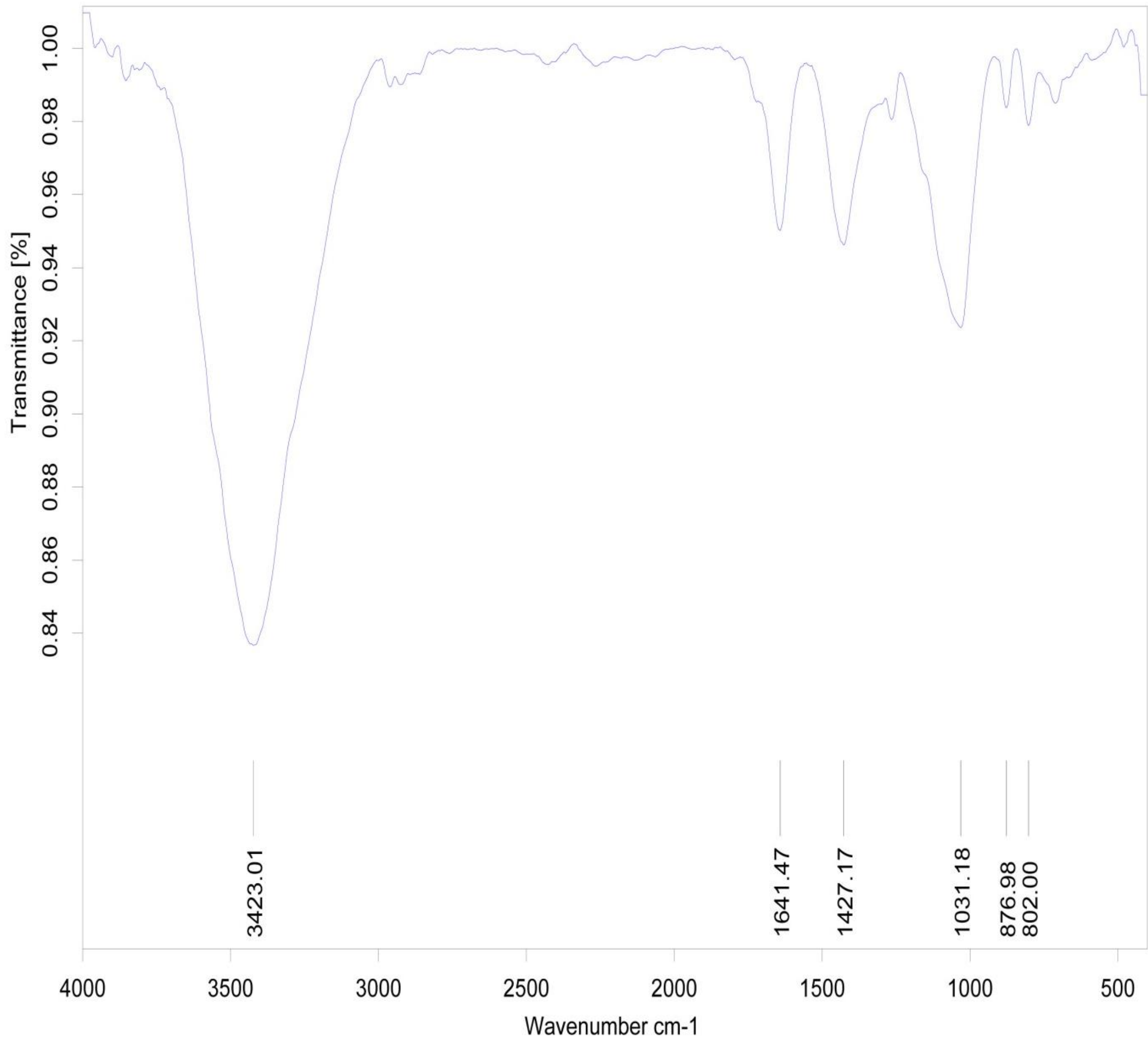
500
Wavenumber cm-1

(j)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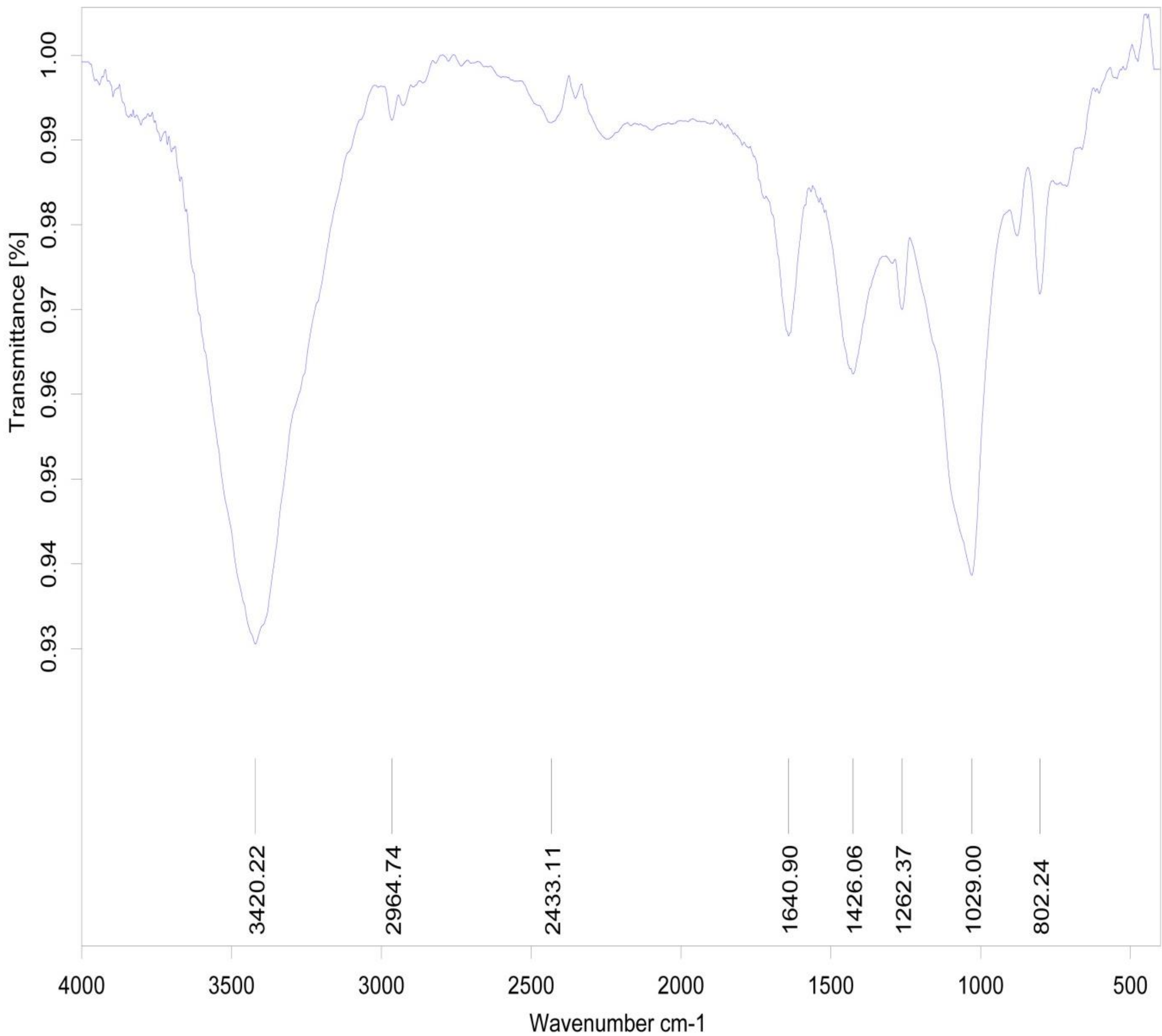
Wavenumber cm-1

(k)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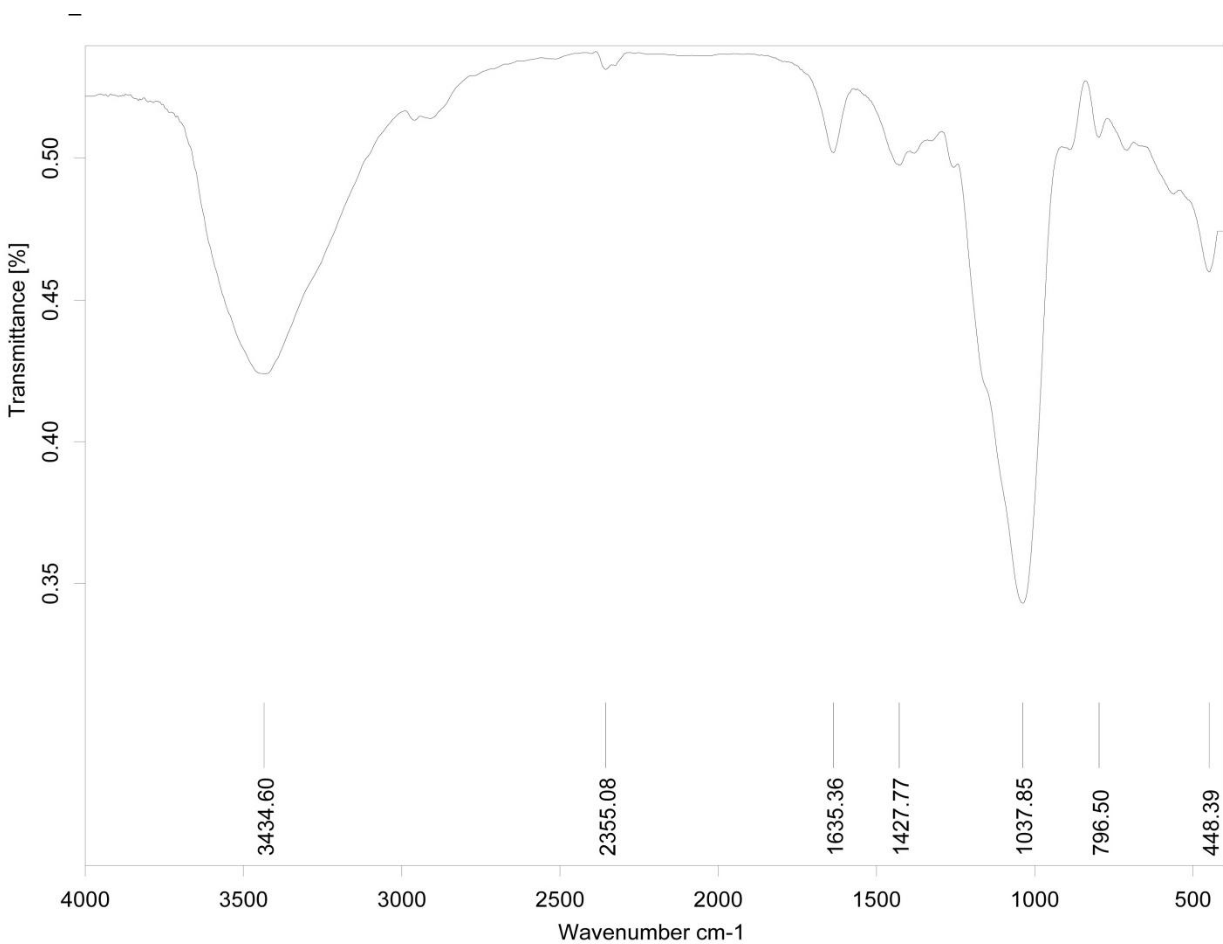
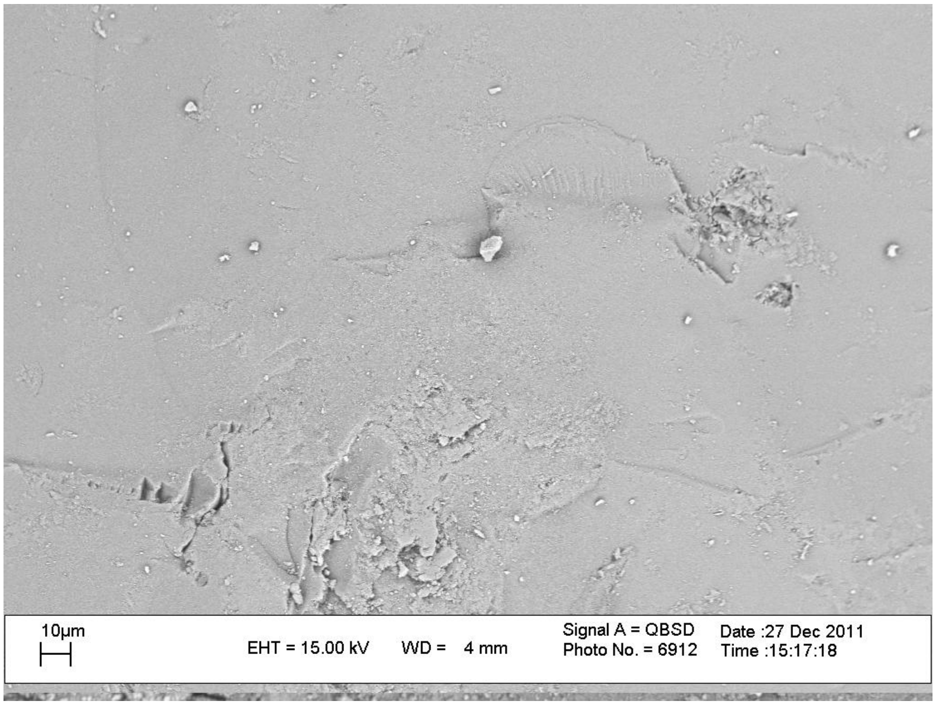
500
Wavenumber cm-1

(l)



(m)

Fig. S10. IR spectra of the Manganese Oxides within Faujasite zeolite for Mn/Zeolite different ratios which that amount of zeolite constant. Contents of manganese in zeolite: a=0.1g, b=0.2g, c=0.3g, d=0.4g, e=0.5g, f=1g, g=2g, h=3g, i=4g, j=5g, k=7g, l=10g, m=Z5D (20g). In all IR spectra: 3420-3440, 1640, 1020-1030 cm^{-1} are assigned to OH stretching, H_2O and the Si-O-(Al)Si vibrations.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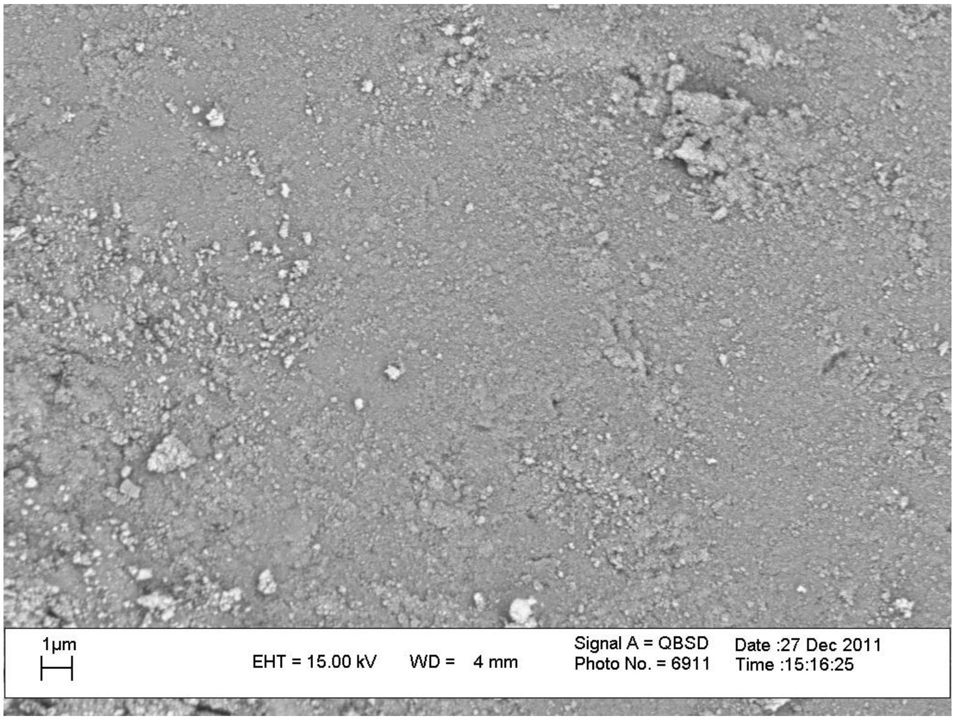
(a)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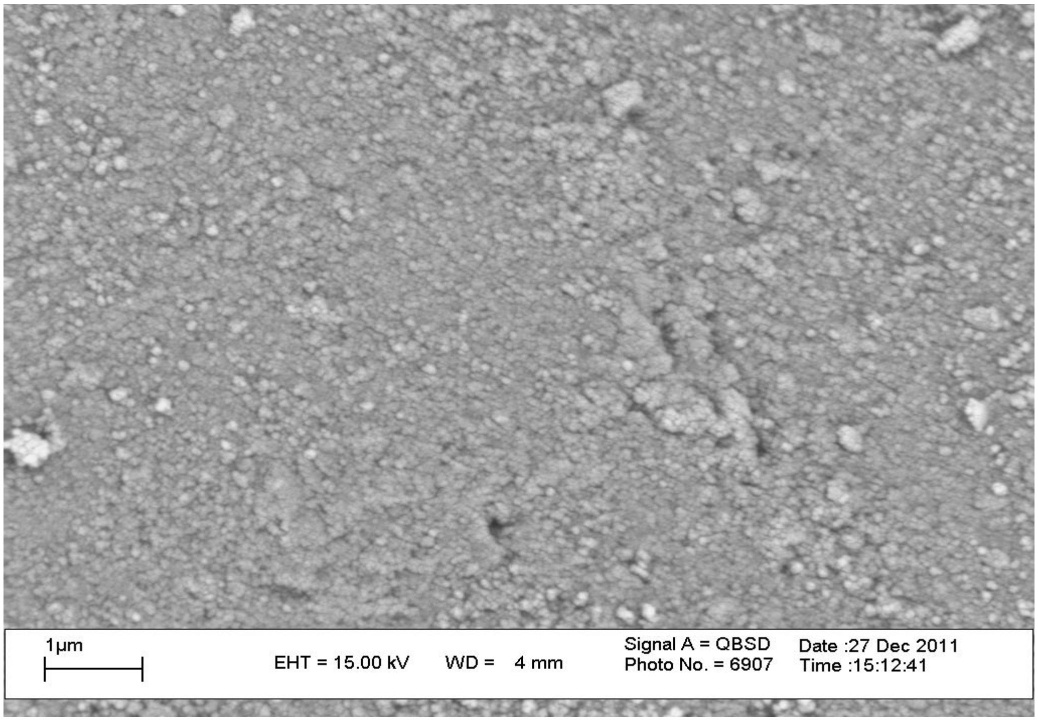
(b)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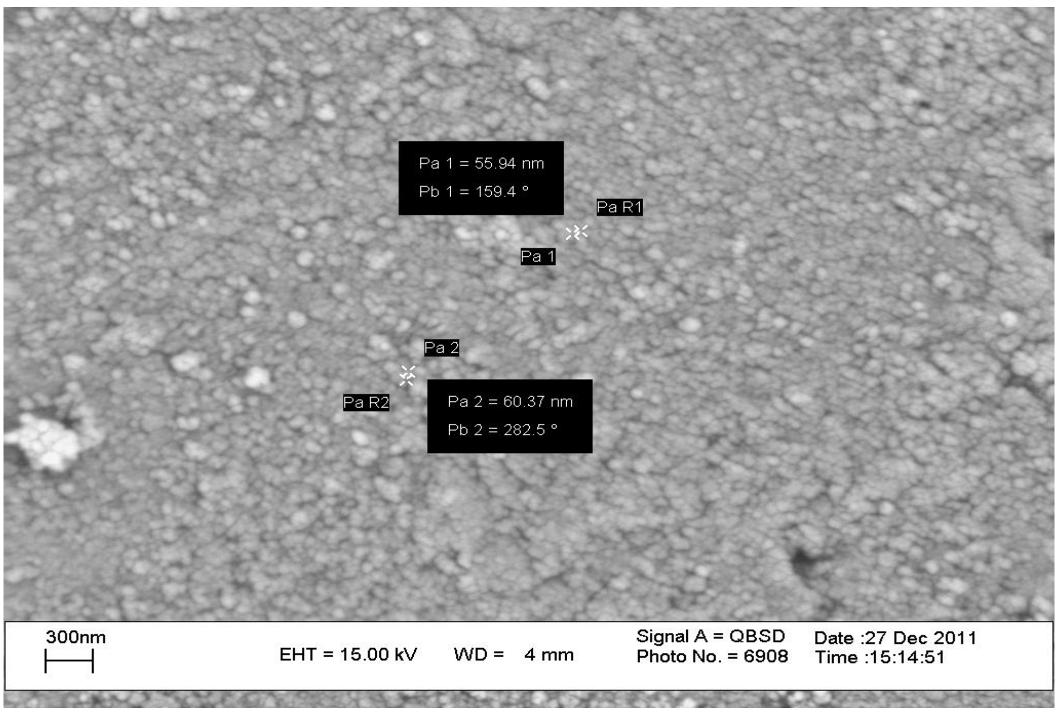
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Pb 1 = 159.4 °
Pa R1
Pa 1
Pa 2
Pa R2
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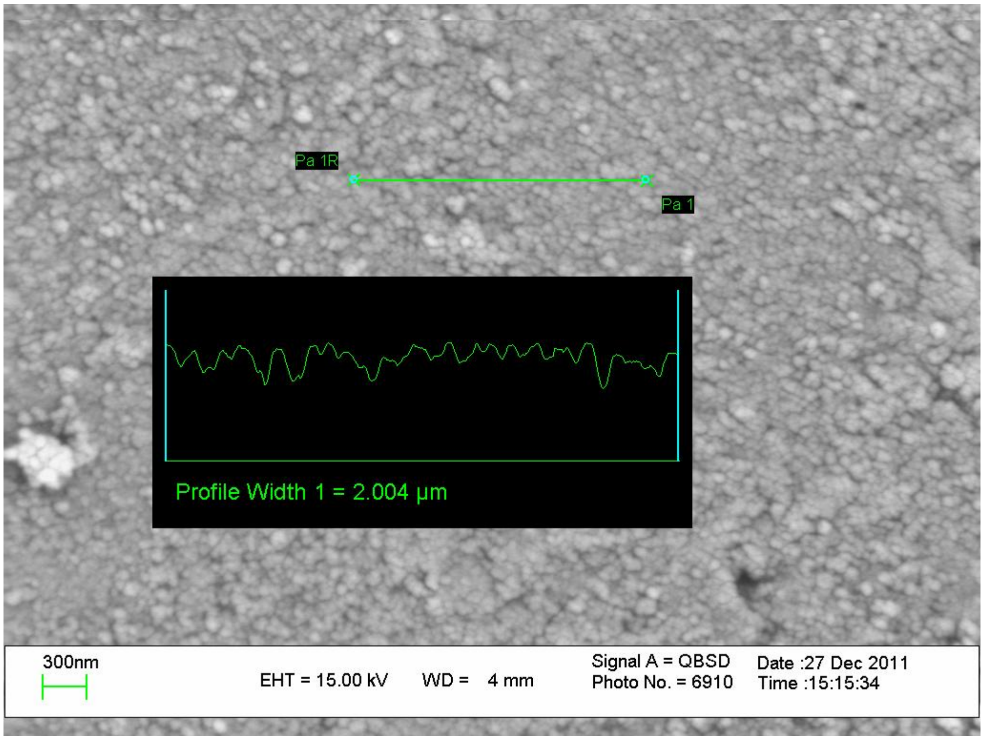
(d)



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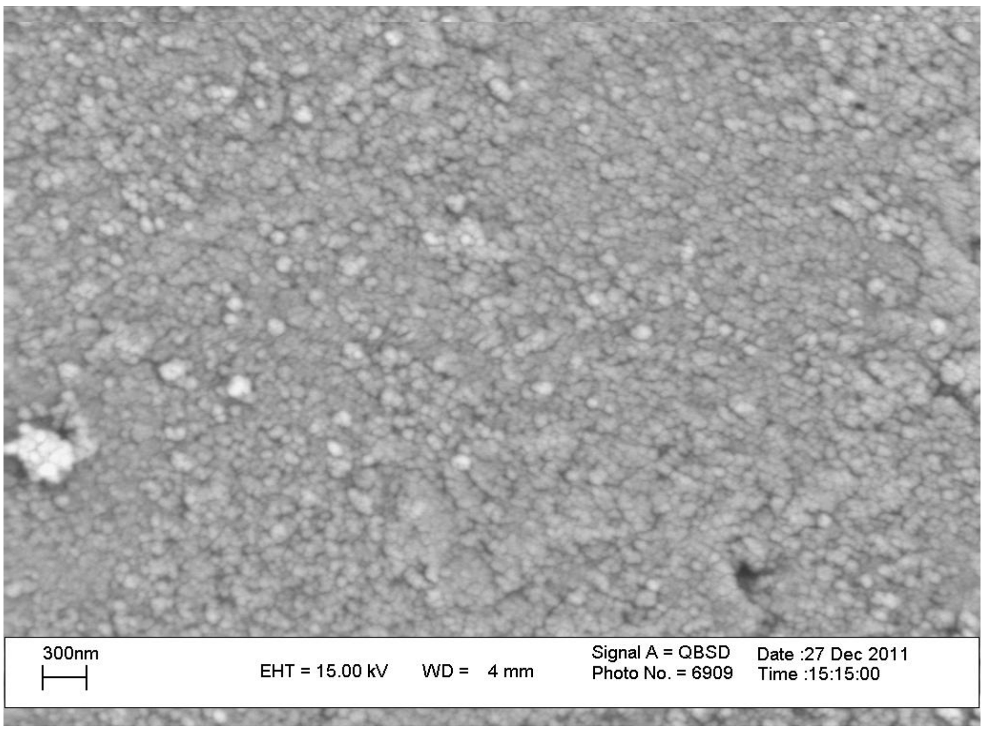
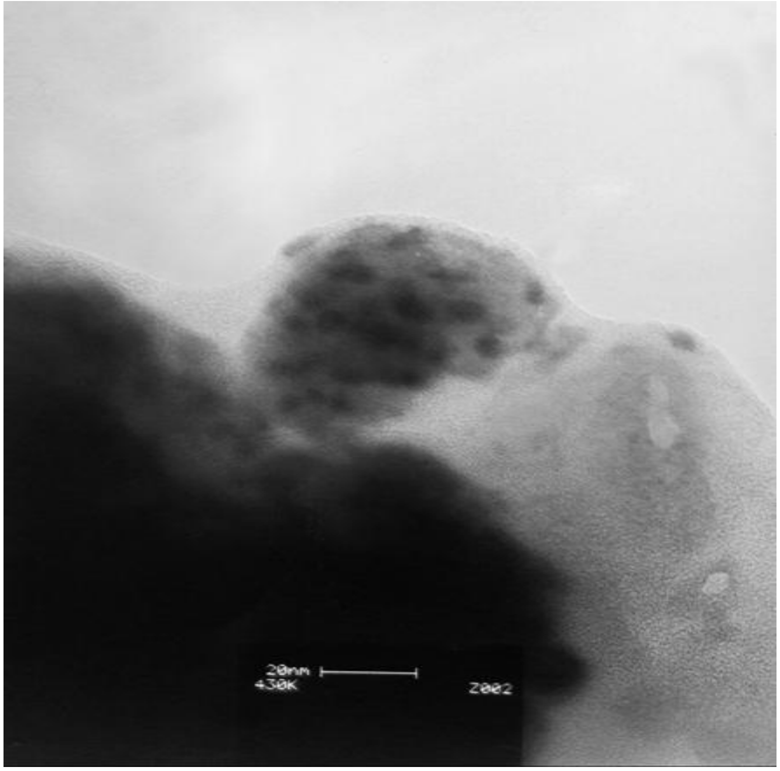
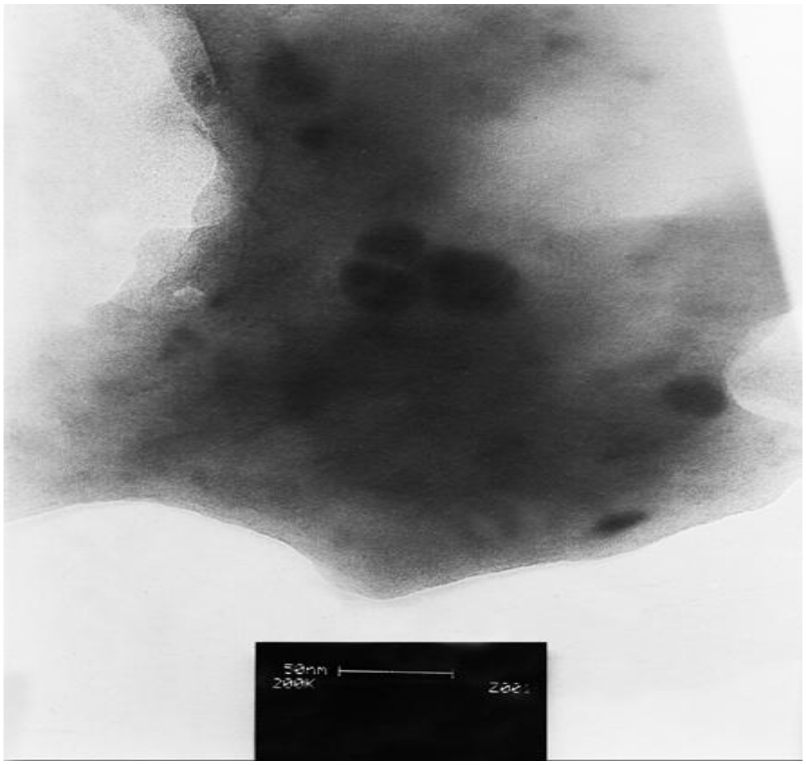


(f)

Fig. S11. SEM images of manganese oxides within Faujasite zeolite (sample of ?) (a-f).



(a)



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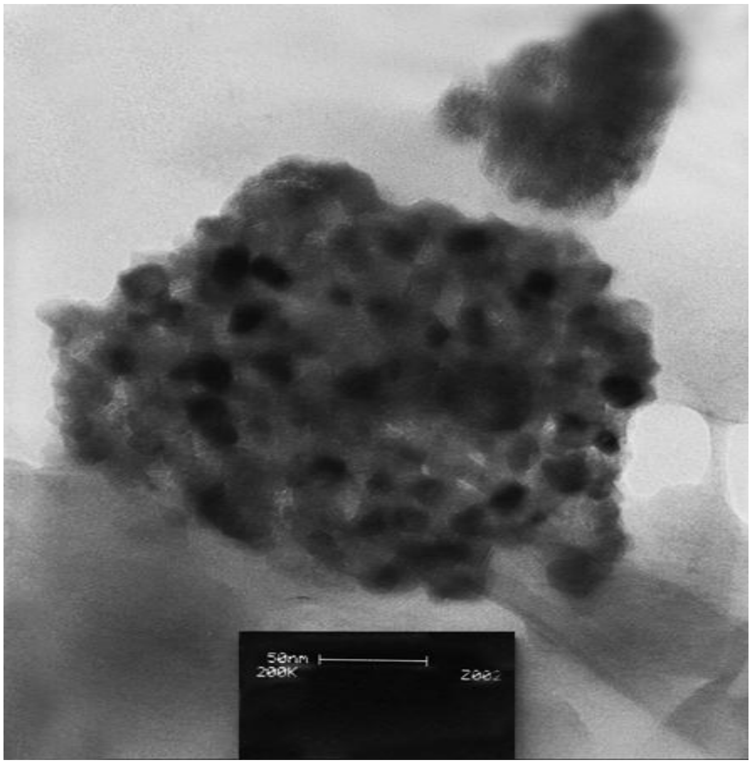
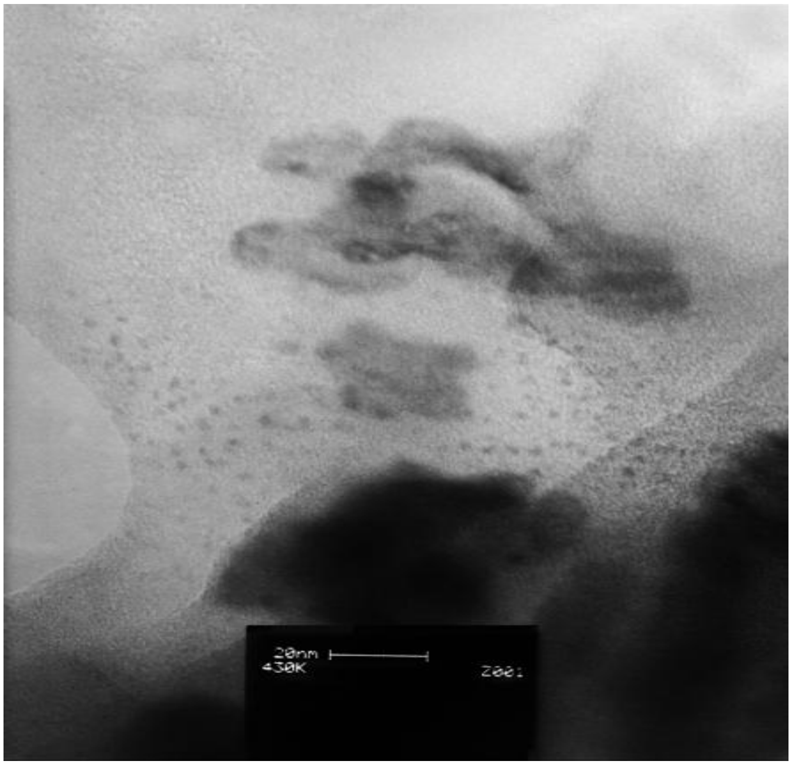
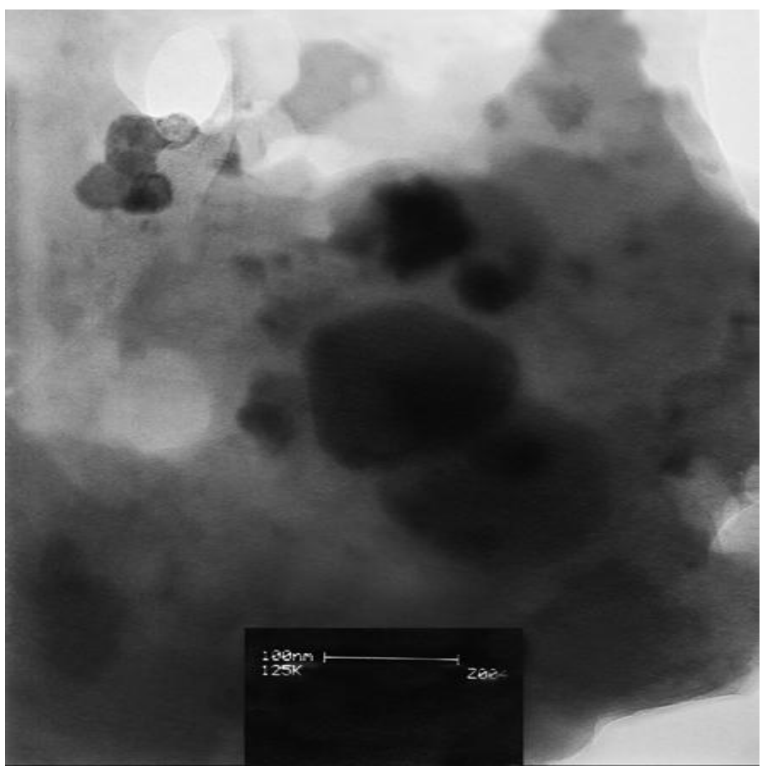


(c)



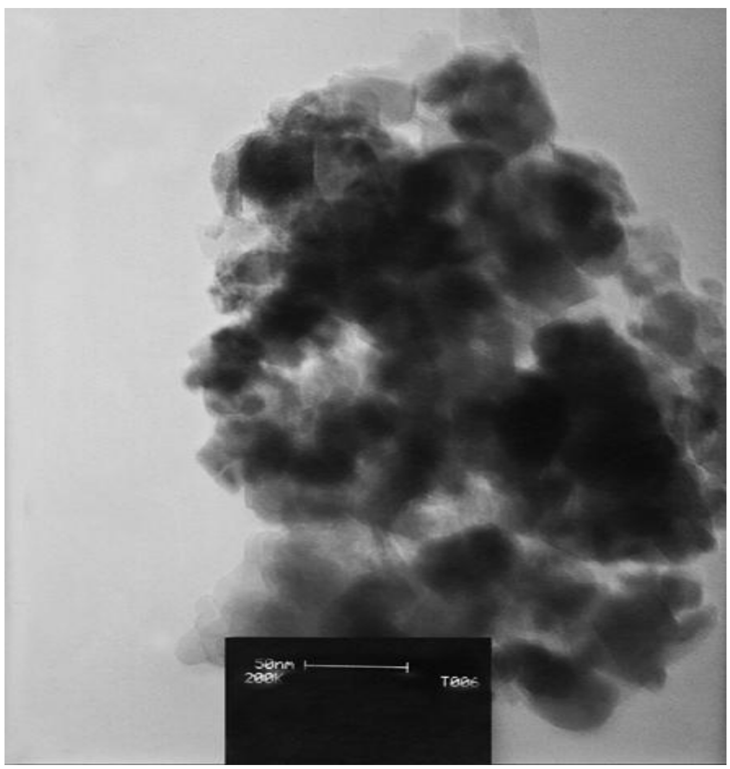
(d)

(e)



(f)

(g)



(h)

Fig. S12. TEM images of manganese oxides within Faujasite zeolite (manganese: 0.5%) (a-h).

Table 2S The rate of water oxidation by the various manganese oxides as catalysts for water oxidation.

Compound	Oxidant	TOF[a] (mmol O_2/mol $Mn.s^{-1}$)	References
Nano scale manganese oxide within NaY zeolite	Ce(IV)	2.62	This Work
$CaMn_2O_4.H_2O$ (Nano particles)	Ce(IV)	2.2	1
$CaMn_2O_4.H_2O$	Ce(IV)	0.54	2
Amorphous Manganese Oxides	$Ru(bpy)_3^{3+}$	0.06	3
	Ce(IV)	0.52	
$CaMn_2O_4.4H_2O$	Ce(IV)	0.32	2
Mn oxide nanoclusters	$Ru(bpy)_3^{3+}$	0.28	4
Nano manganese oxide - Bovine Serum Albumin	$Ru(bpy)_3^{3+}$	0.14	5
	Ce(IV)	0.27	
Nano-sized α-Mn_2O_3	Ce(IV)	0.15	6
Octahedral Molecular Sieves	$Ru(bpy)_3^{3+}$	0.11	3
	Ce(IV)	0.05	
MnO_2 (colloid)	Ce(IV)	0.09	7
α-MnO_2 nanowires	$Ru(bpy)_3^{3+}$	0.059	8
$CaMn_3O_6$	Ce(IV)	0.046	9
$CaMn_4O_8$	Ce(IV)	0.035	9
α-MnO_2 nanotubes	$Ru(bpy)_3^{3+}$	0.035	8
Mn_2O_3	Ce(IV)	0.027	2
β-MnO_2 nanowires	$Ru(bpy)_3^{3+}$	0.02	8
$Ca_2Mn_3O_8$	Ce(IV)	0.016	10
$CaMnO_3$	Ce(IV)	0.012	10
Bulk α-MnO_2	$Ru(bpy)_3^{3+}$	0.01	8
PSII	Sunlight	10^5-4×10^5	11

References:

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