Supplementary Information

Synthesis of $MnFe_2O_4$ @SiO_2@CeO_2 and Applications in Water Remediation

Garret Dee[α], Hend Shayoub[α], Helen McNeill[α], Itziar Sánchez Lozano[β], Aran Rafferty[α] and Yurii K. Gun'ko[α]*

[α] School of Chemistry, University of Dublin, Trinity College, Dublin 2, Ireland

[β] Universidad de Alcalá de Henares, Facultad de Ciencias Químicas, Spain

* Corresponding Author (Y.G.) E-mail: igounko@tcd.ie

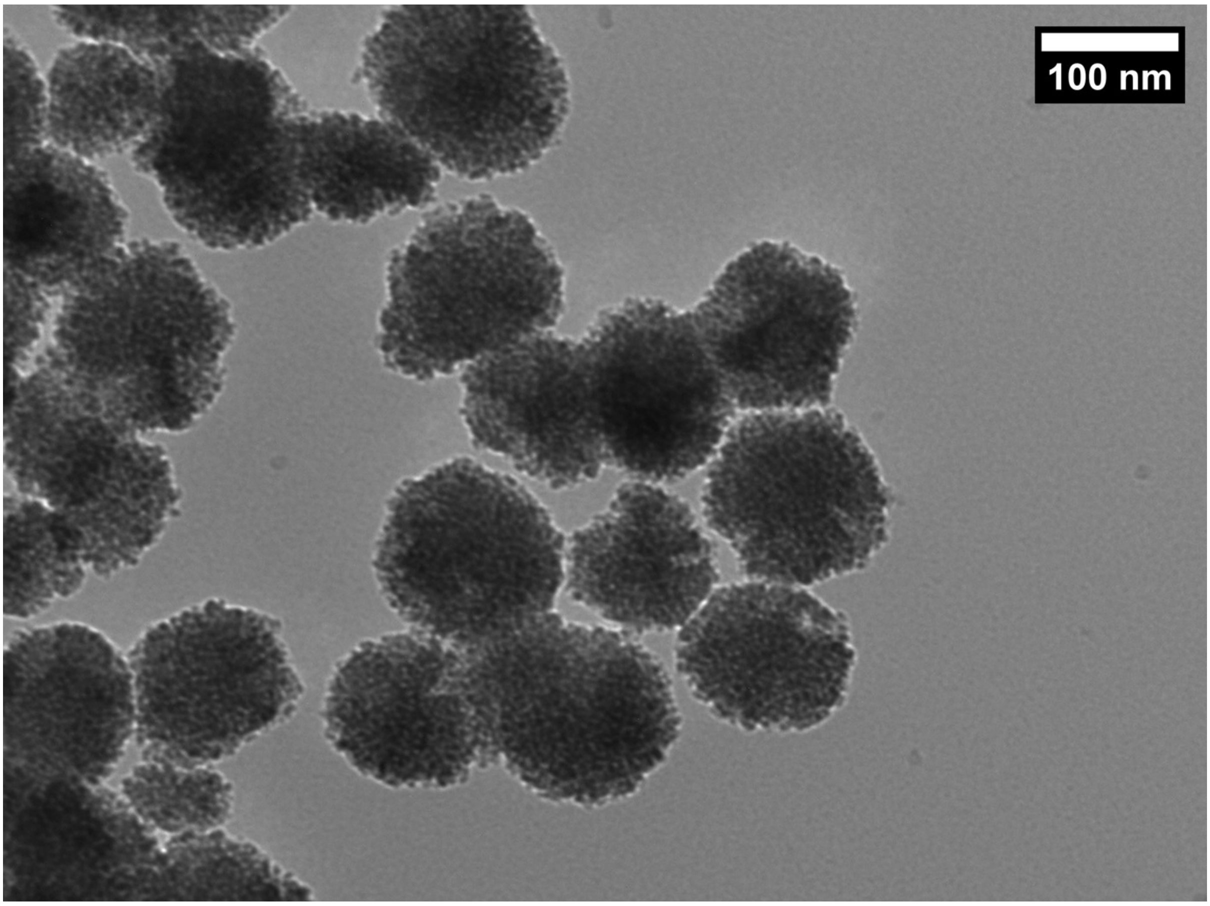

Figure S1: TEM image of Manganese Ferrite cores showing grain structure of particles.

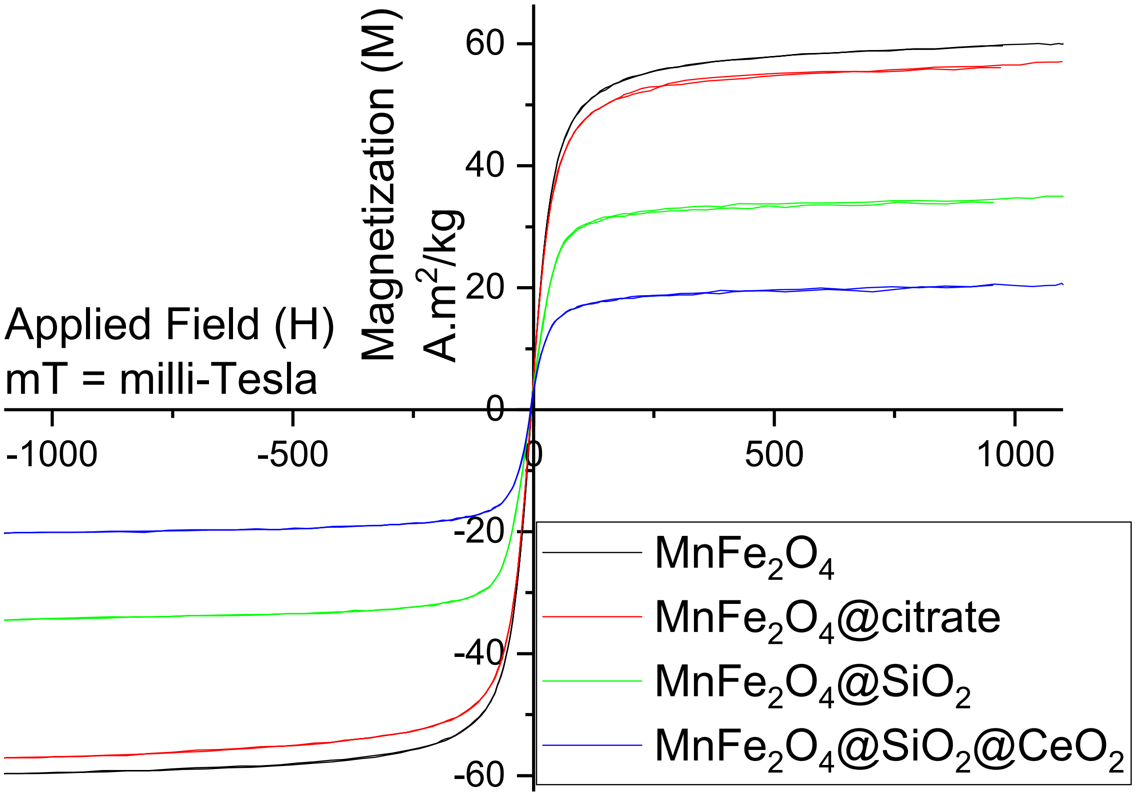

Figure S2: VSM of the various synthesised particles.

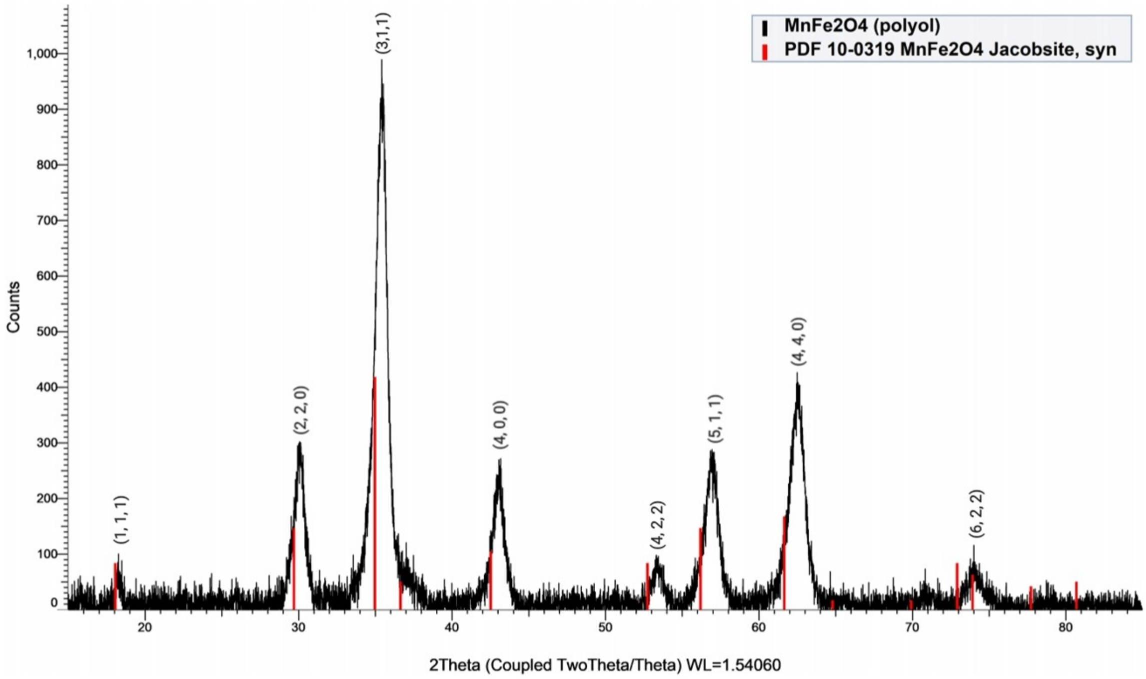

Figure S3: XRD analysis of the Manganese Ferrite core particles.

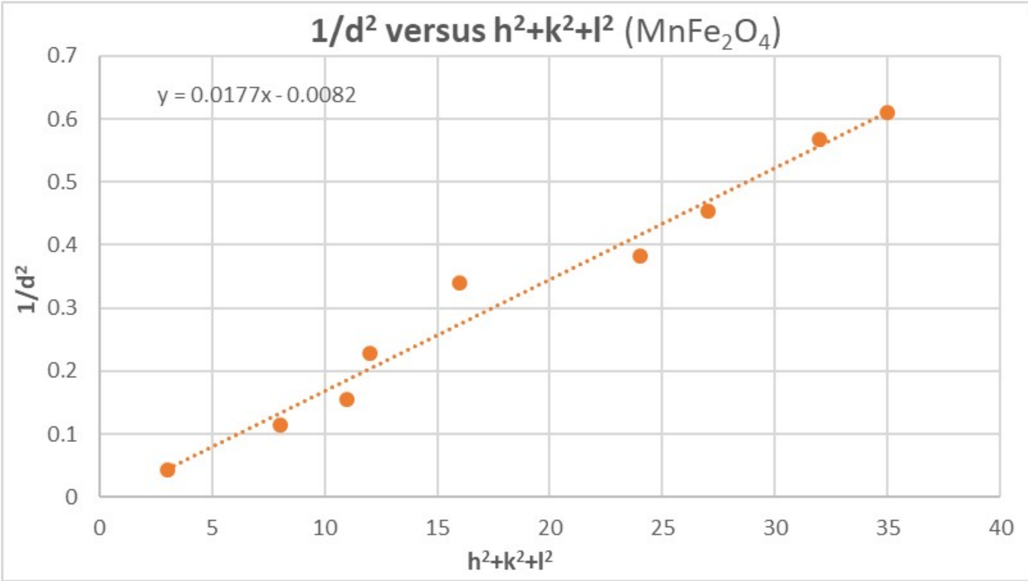

Figure S4: Plot of data from peaks of XRD of manganese ferrite core to give the lattice constant. The lattice constant, a = 1/slope. Therefore a = 7.522 Å.

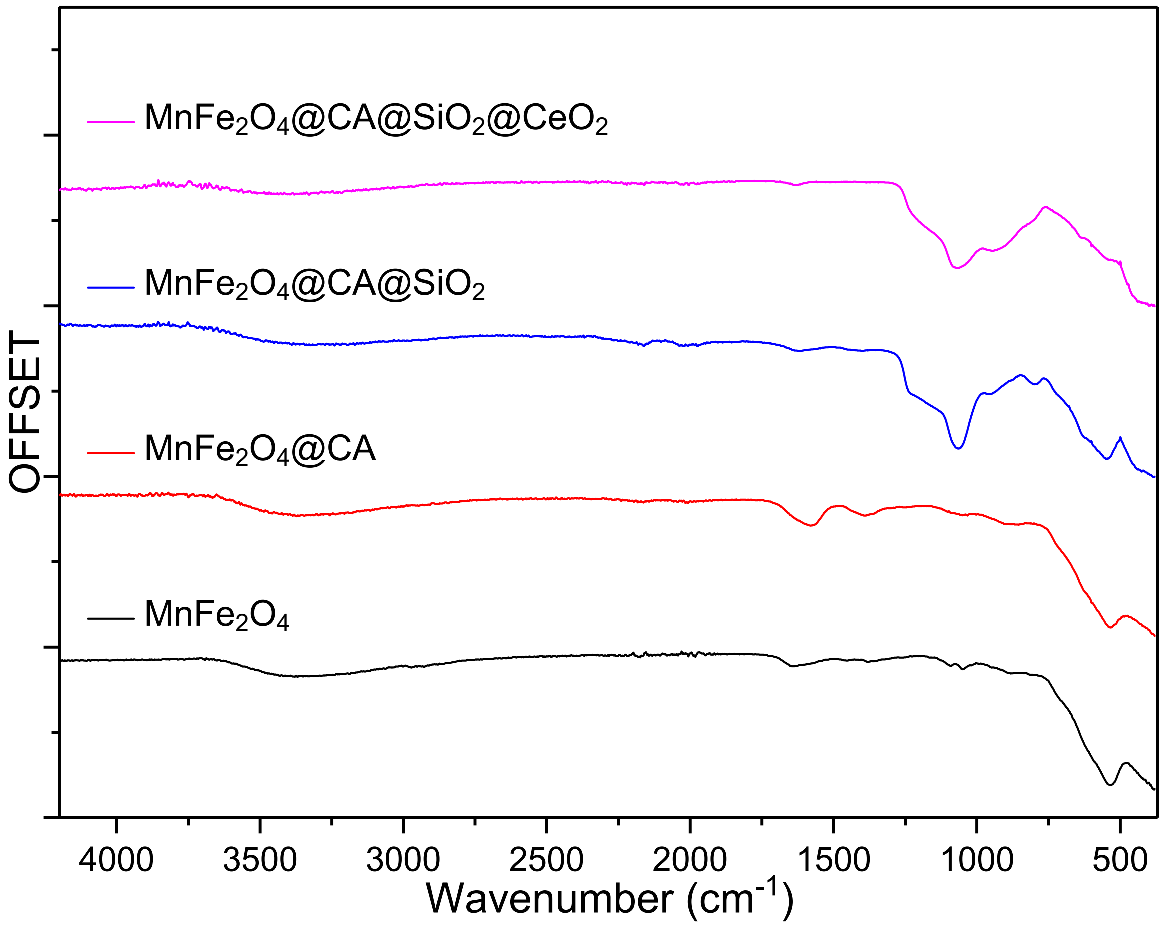

Figure S5: FTIR of the various synthesised nanostructures.

Table S1: DLS measurements for $MnFe_2O_4$ cores,the citrate stabilised MNPs and the Silica coated MNPs suspension showing the Z-Average, the PolyDispersity Index (PDI) and the Count Rate.

	$MnFe_2O_4$			$MnFe_2O_4$@citrate			$MnFe_2O_4@SiO_2$		
Time	**Z-Average**	**PDI**	**Count Rate**	**Z-Average**	**PDI**	**Count Rate**	**Z-Average**	**PDI**	**Count Rate**
	d.nm		**kcps**	**d.nm**		**kcps**	**d.nm**		**kcps**
0 hr	221.3	0.197	215994	184.1	0.082	78296	221.8	0.023	50651
1 hr	242.7	0.242	227036	187.5	0.062	77056	219.0	0.028	50098
2 hr	258.9	0.272	224937	181.9	0.043	80535	221.4	0.065	49719
3 hr	236.4	0.21	198558	182.9	0.086	72957	221.2	0.054	49009
5 hr	255.2	0.254	189360	184.4	0.093	74890	221.3	0.007	48675
1 day	314.4	0.254	152362	180	0.072	72701	224.3	0.002	48329
2 day	290.6	0.25	106426	180.6	0.086	63751	217.4	0.003	59226
3 day	213.2	0.125	69809	175.6	0.071	48604	218.5	0.056	59780
5 day	217.1	0.097	45751	172.3	0.074	34912	210.7	0.008	44100
7 day	184.1	0.115	26553	176.3	0.044	28191	212.9	0.03	17870

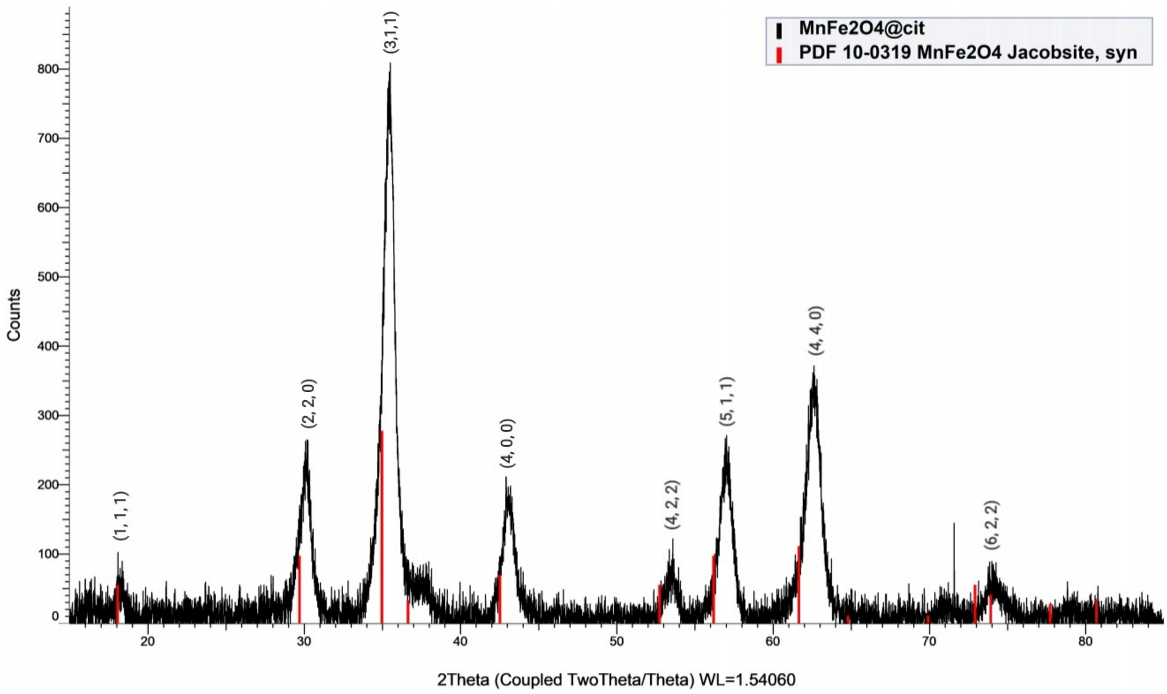

Figure S6: XRD of the citrate stabilised manganese ferrite cores.

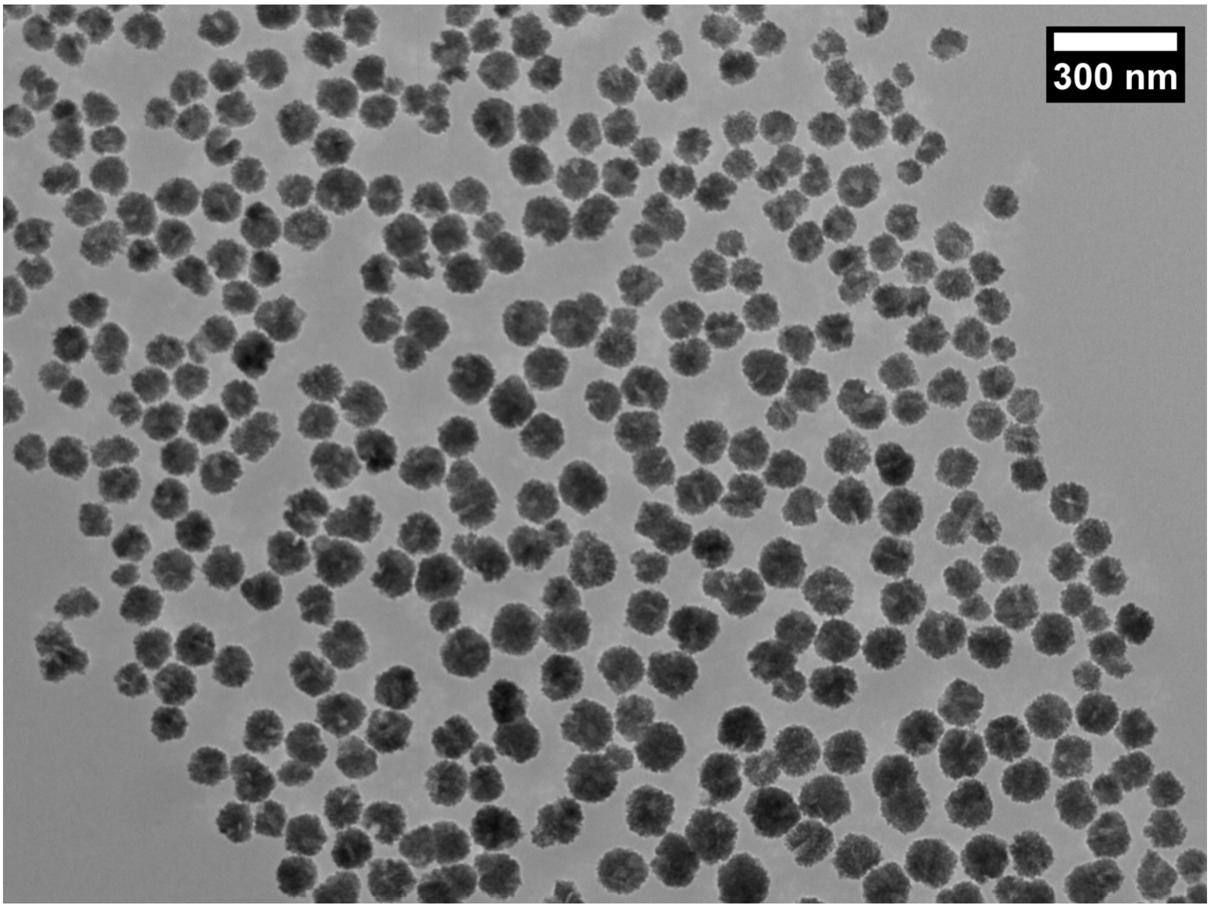

Figure S7: TEM image of the citrate stabilised manganese ferrite cores.

$$\frac{\left(\frac{core\ diameter}{2} + shell\ thickness\right)^3 - \left(\frac{core\ diameter}{2}\right)^3}{\left(\frac{core\ diameter}{2}\right)^3} = volume\ shell{:}core$$

Equation S1: The ratio of the volume of the core to the volume of the shell for one MNP is calculated knowing the size of the core (TEM images)

$$volume\ shell{:}core\left(\frac{density\ of\ shell\ material}{density\ of\ core\ material}\right) = mass\ shell{:}core$$

Equation S2: From equation 1, the ratio of the mass of the shell to the mass of the MNP is calculated knowing the densities of each material

$$mass\ shell{:}core\left(\frac{molar\ mass\ of\ core\ material}{molar\ mass\ of\ shell\ material}\right) = moles\ of\ shell{:}core$$

Equation S3: From equation 2, the mole ratio of shell to core can be calculated knowing the molar masses of the materials and precursors. Then knowing the number of mass of core used as precursor the number of moles of shell precursor can be calculated

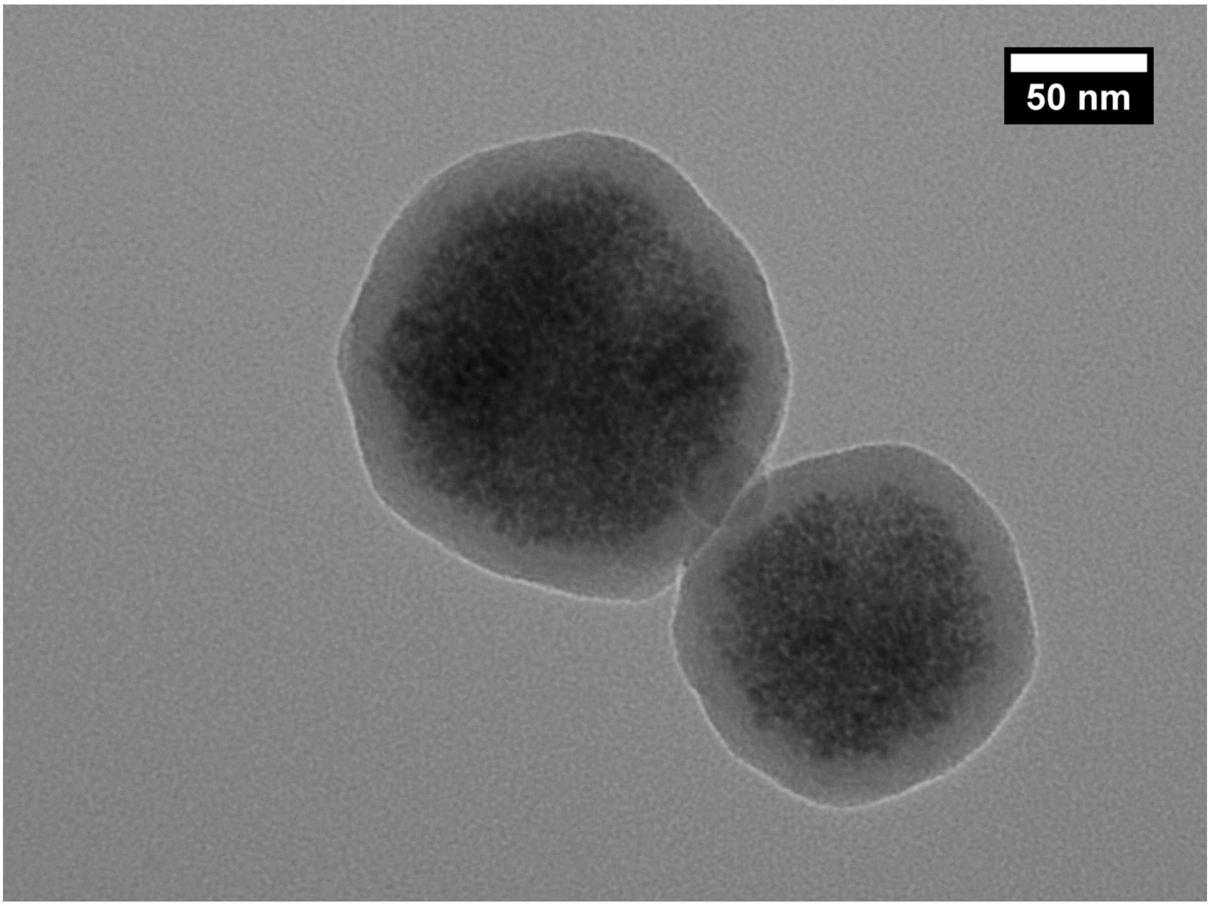

Figure S8: TEM image of the SiO_2 coated $MnFe_2O_4$ magnetic cores.

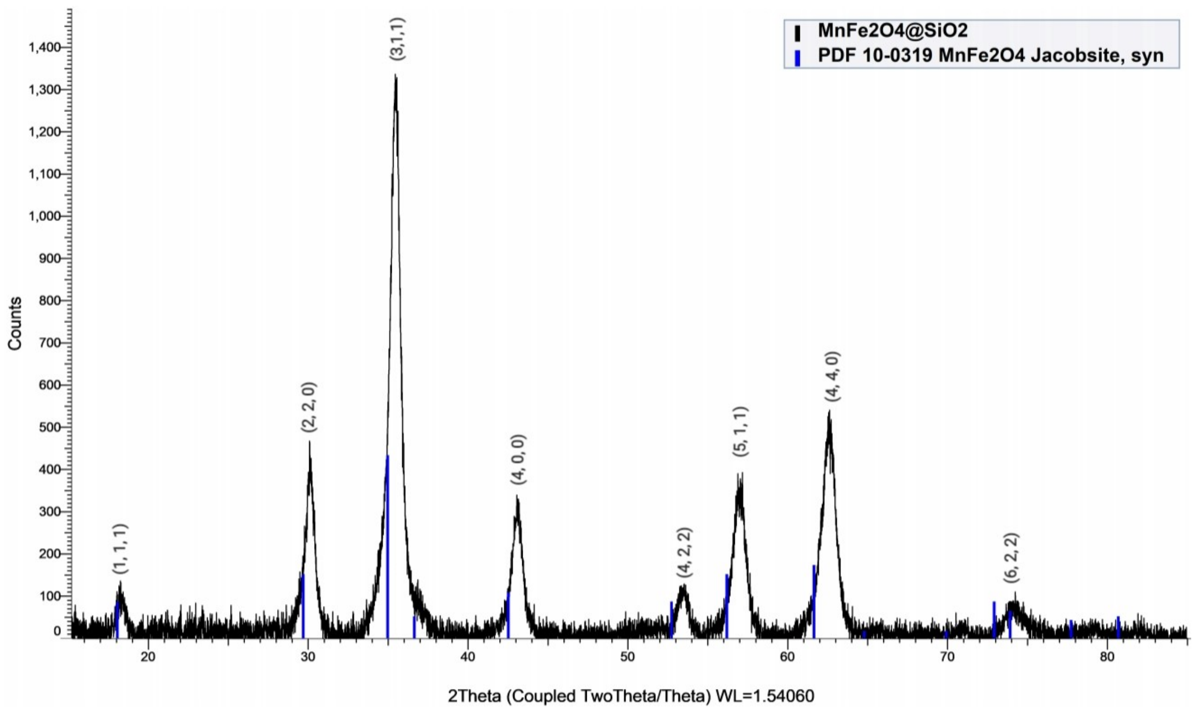

Figure S9: XRD analysis of the $MnFe_2O_4$@SiO_2 particles.

$$\frac{volume\ of\ core(density\ of\ core) + volume\ of\ shell1(density\ of\ shell1)}{volume\ of\ core + volume\ of\ shell1}$$

Equation S4: To calculate the density of the $MnFe_2O_4@SiO_2$ so the amount of CeO_2 precursor can be calculated using Equation S1-S3

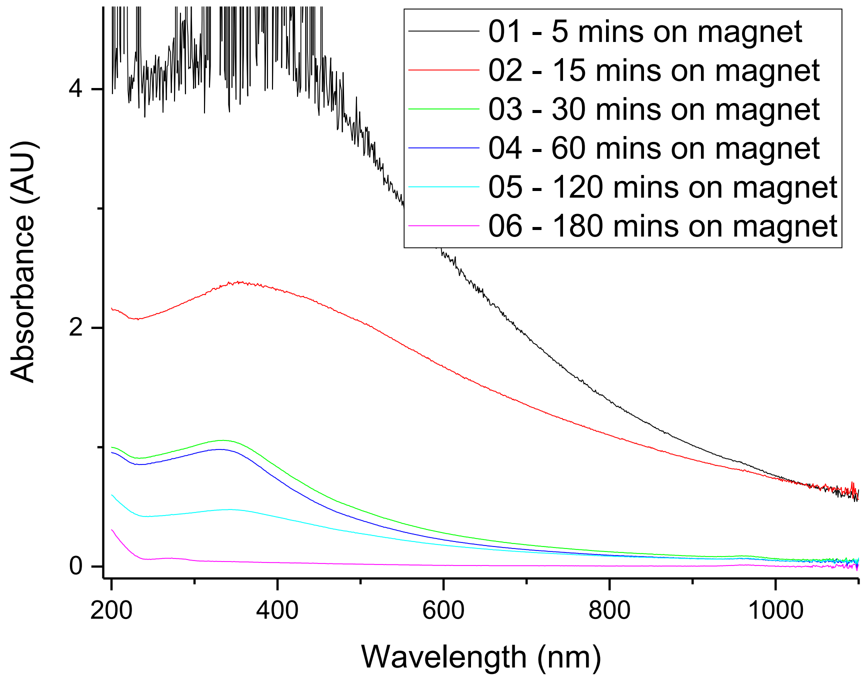

Figure S10: Reduction in absorbance as the CeO_2 coated particles are magnetically extracted from solution and the solution becomes clear.

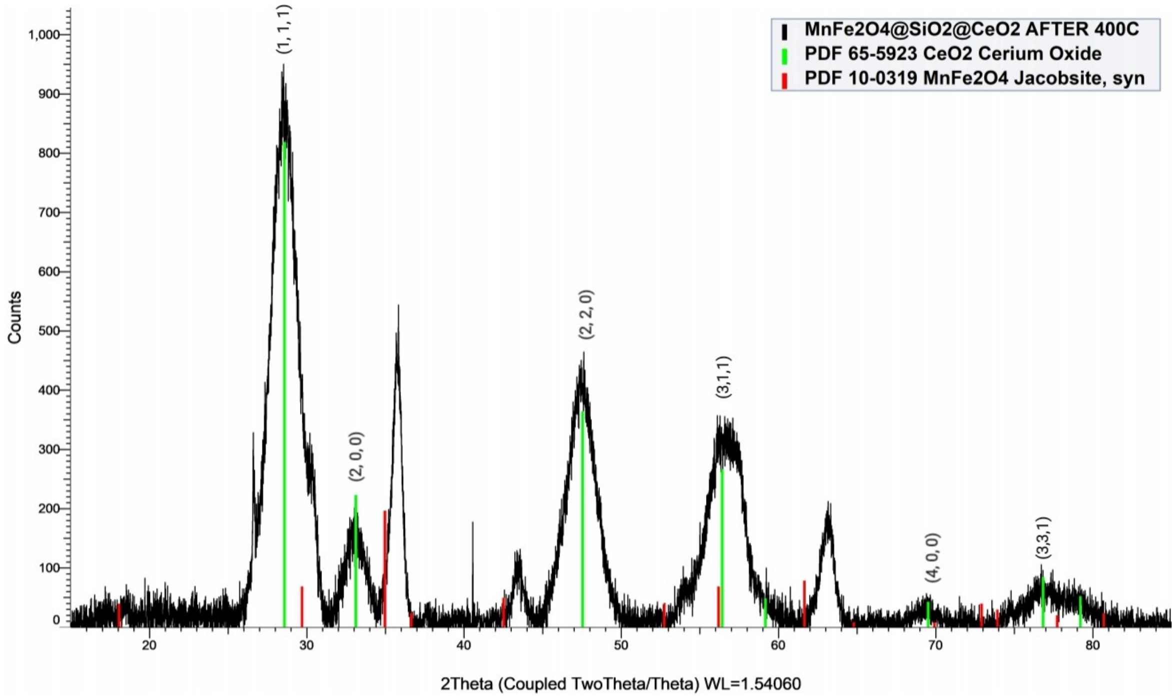

Figure S11: XRD analysis of the $MnFe_2O_4@SiO_2@CeO_2$ particles showing a match for CeO_2.

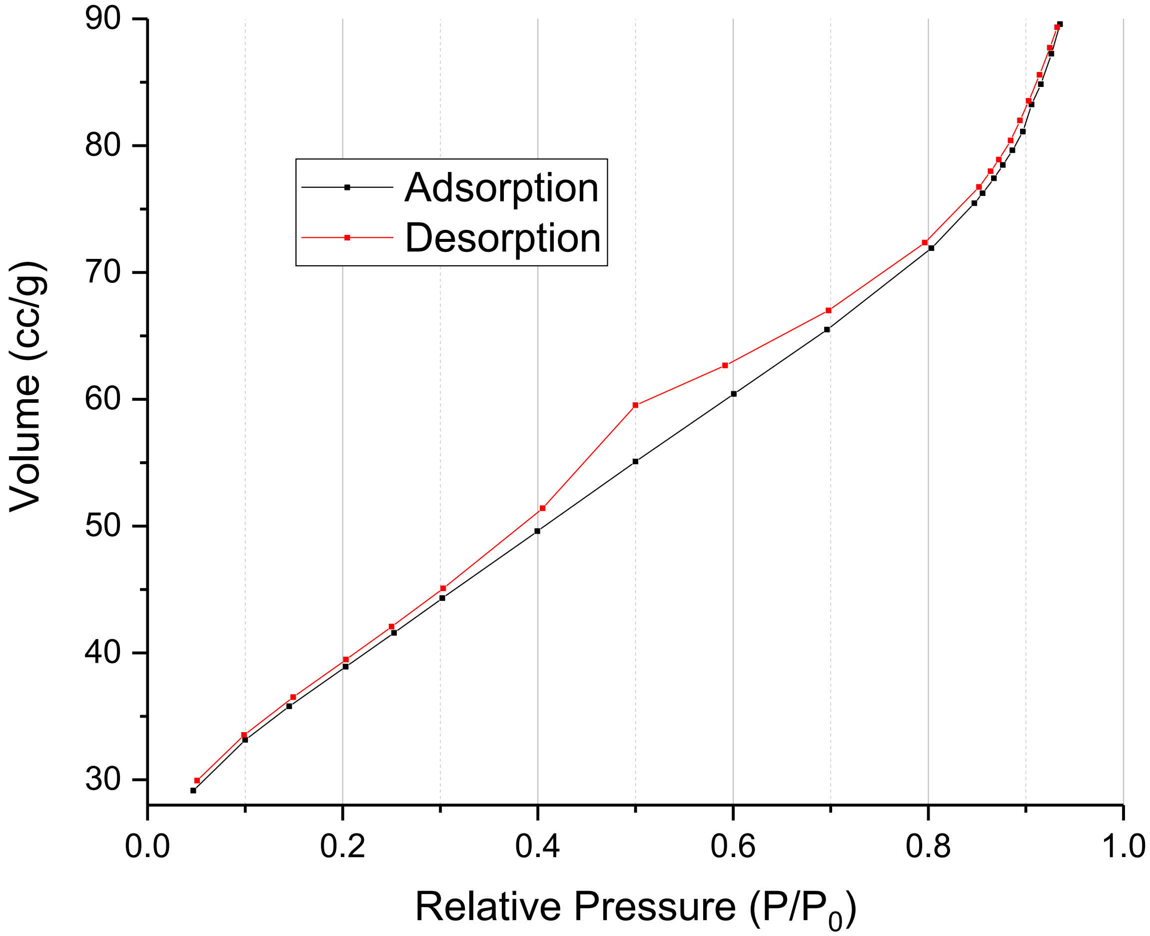

Figure S12: Nitrogen adsorption-desorption isotherm for the CeO_2 coated MNPs.

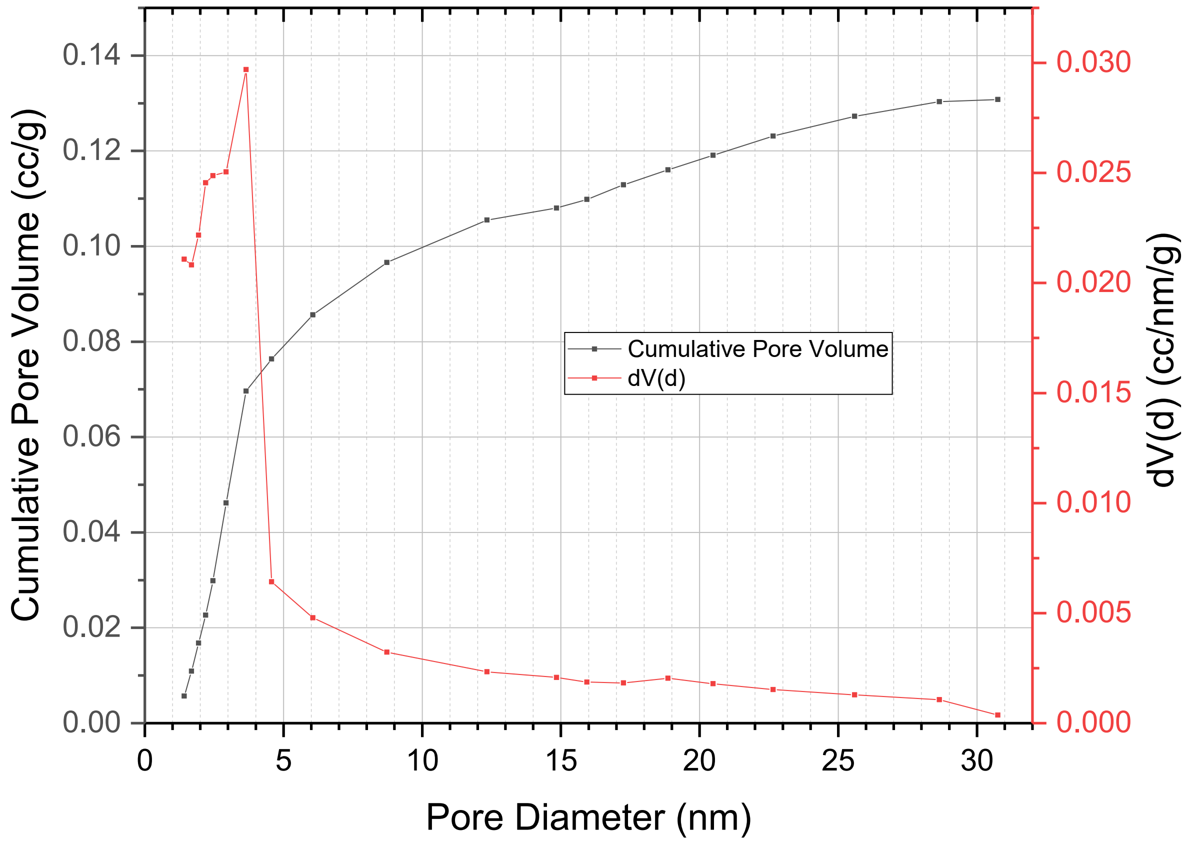

Figure S13: BJH pore size distribution of the ceria-coated magnetic nanoparticles.

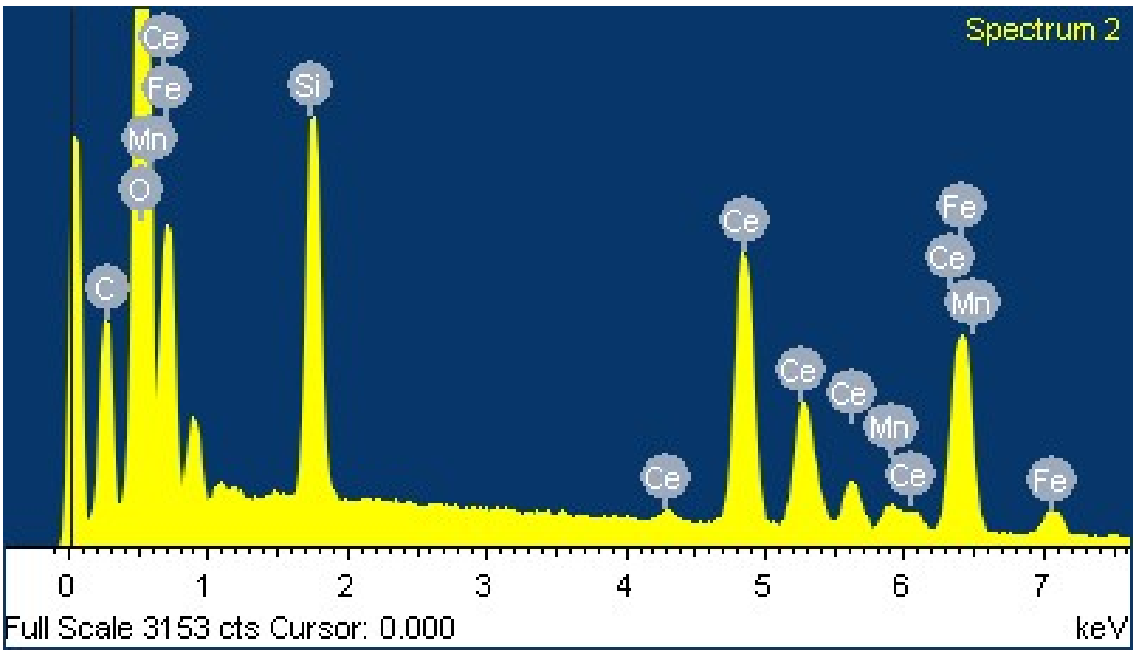

Figure S14: EDX of the ceria coated nanoparticles. The carbon peak comes from the sample holder.

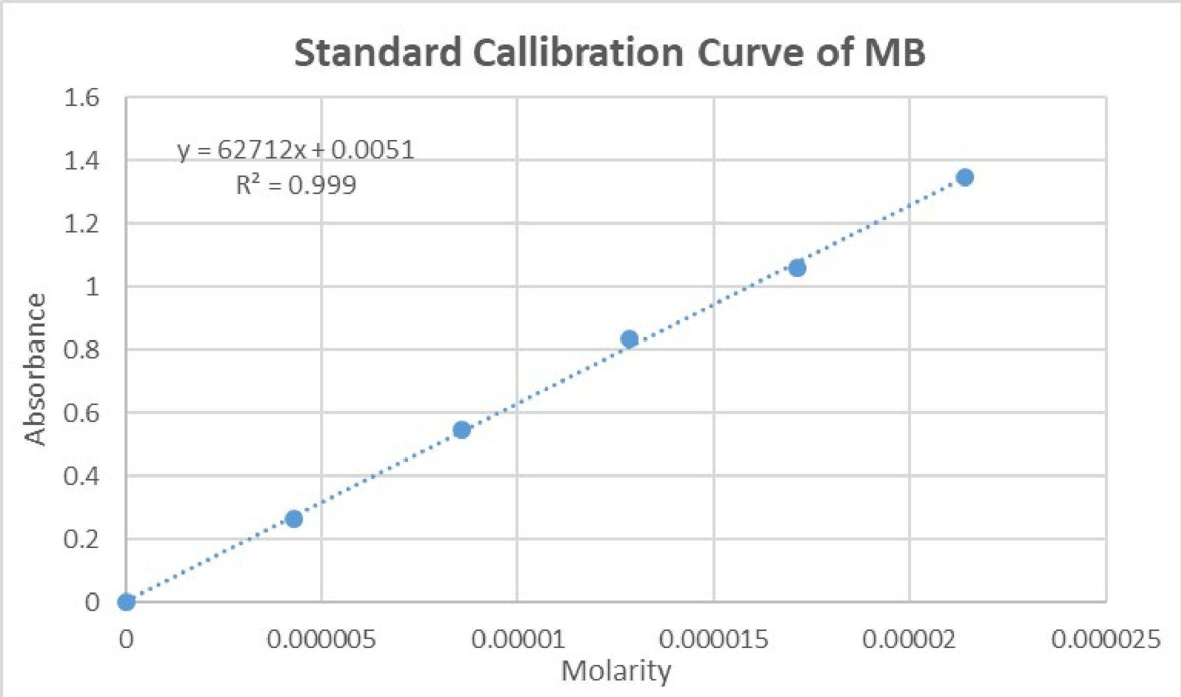

Figure S15: Standard Calibration Curve for Methylene Blue dye solution, which calculates the molar attenuation coefficient to be 62712 L mol^{-1} cm^{-1}.

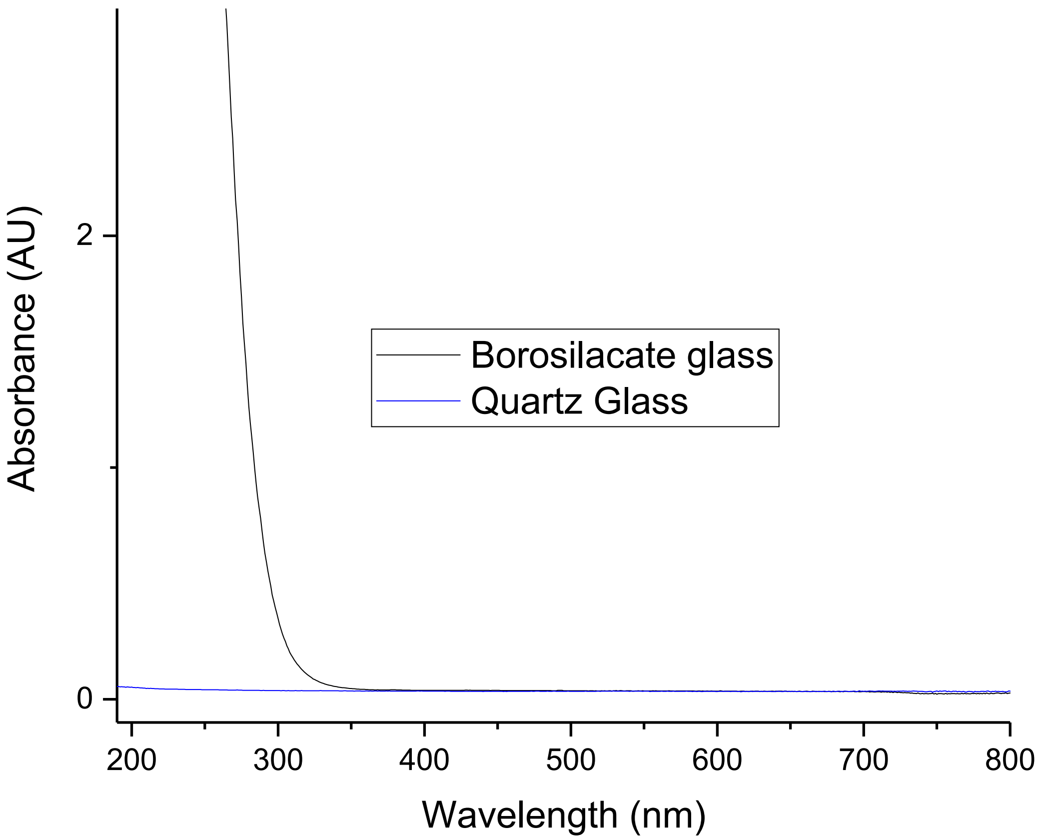

Figure S16: UV-vis spectra of Quartz glass and Borosilicate glass showing the cut-off in the UV region.

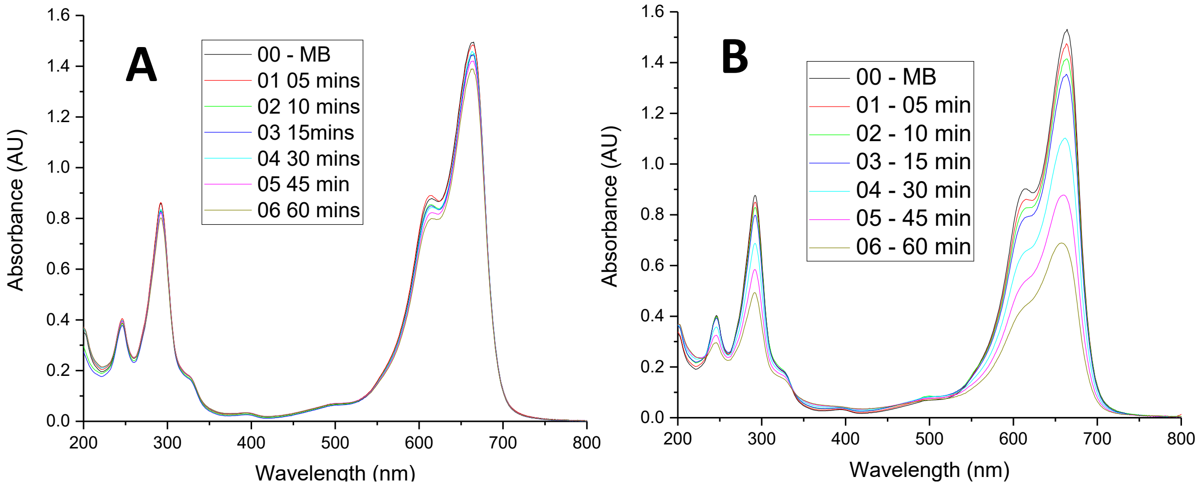

Figure S17: UV-vis spectra showing (A) degradation of MB with light above 360 nm and (B) degradation of MB with light above 190 nm.

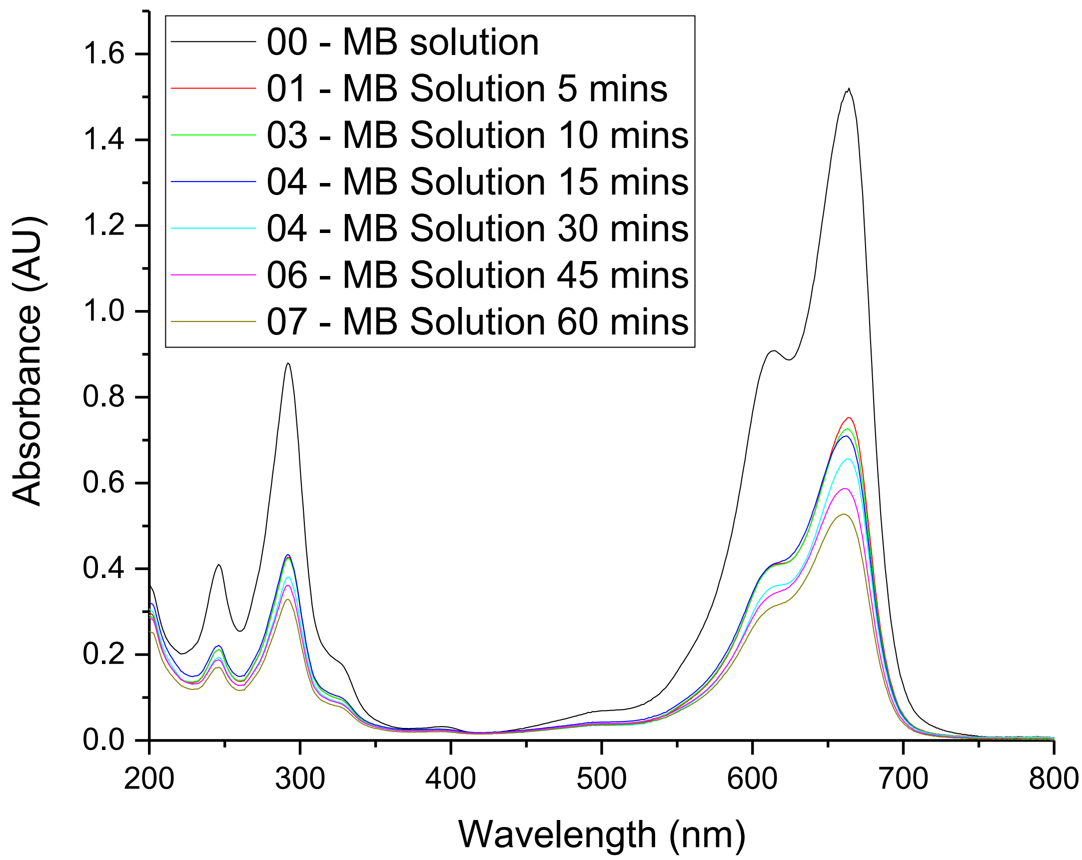

Figure S18: UV-vis spectrum showing adsorption and photo-degradation.

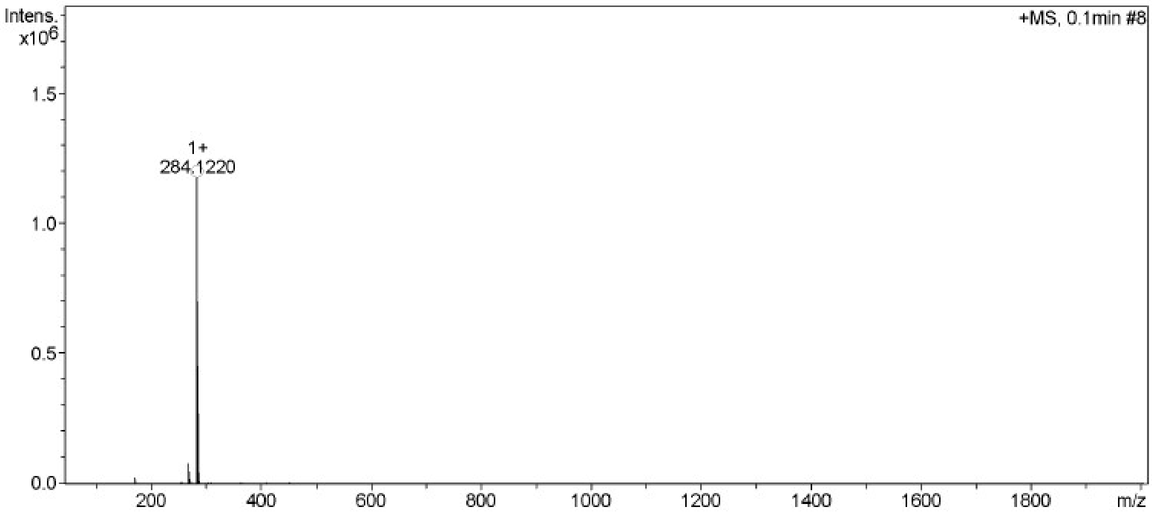

Figure S19: MS of the MB solution before any experiments.

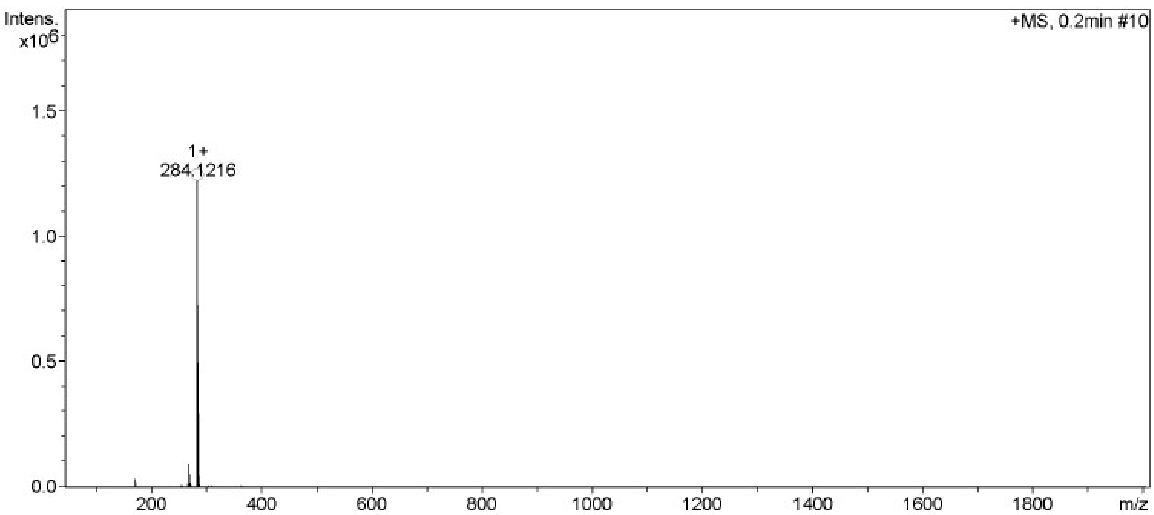

Figure S20: MS of the MB solution after experiment involving only adsorption.

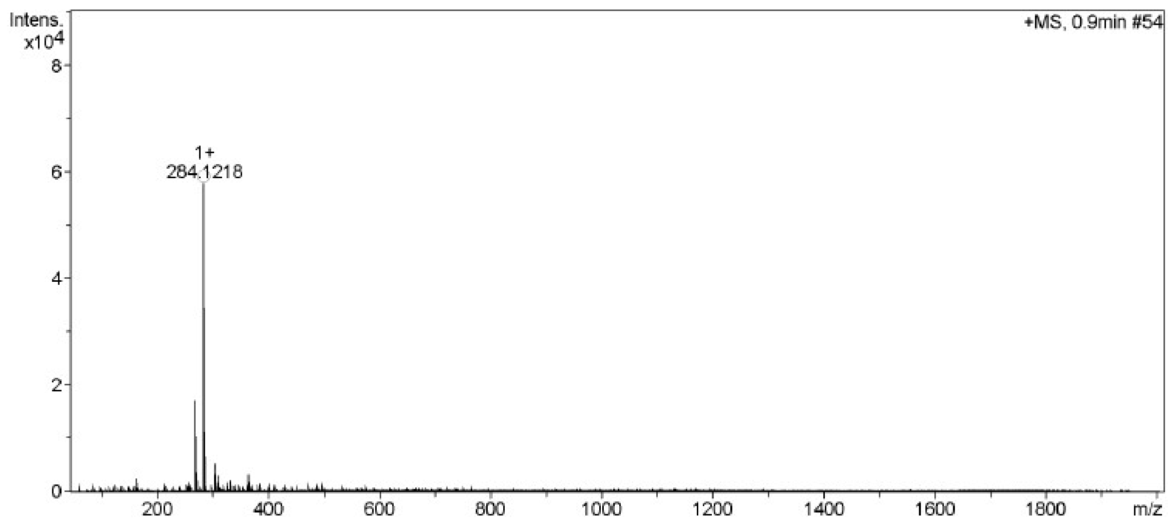

Figure S21: MS of MB solution after experiment involving adsorption and photo-degradation.

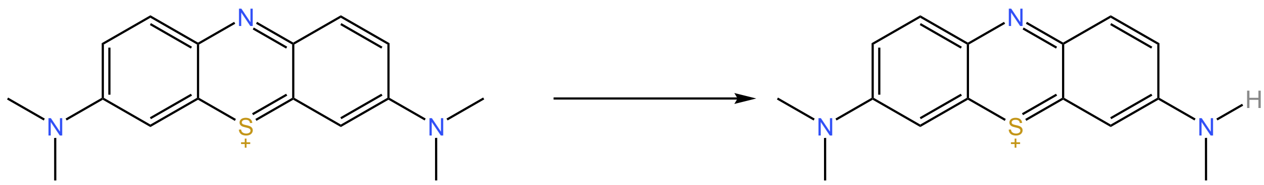

Figure S22: Photo-degradation product of MB.

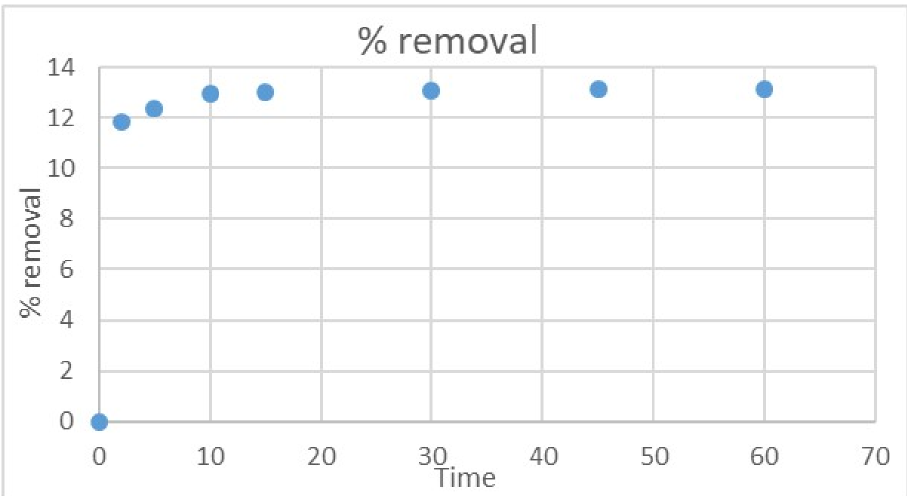

Figure S23: MB removal from 200 ml of a 10 mg/L solution with 50 mg MNPs over 1 hour.

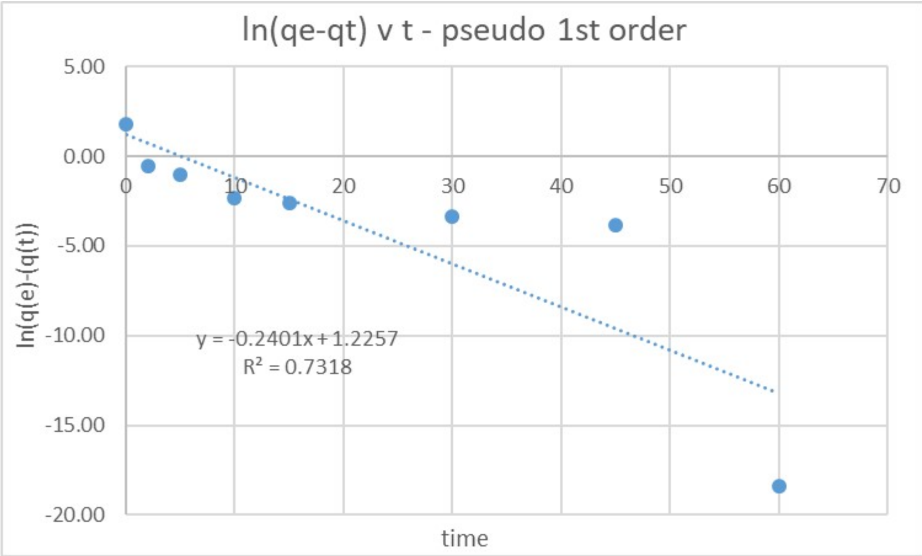

Figure S24: Pseudo first order kinetics for 200 ml of a 10 mg/L with 50 mg MNPs over 1 hour.

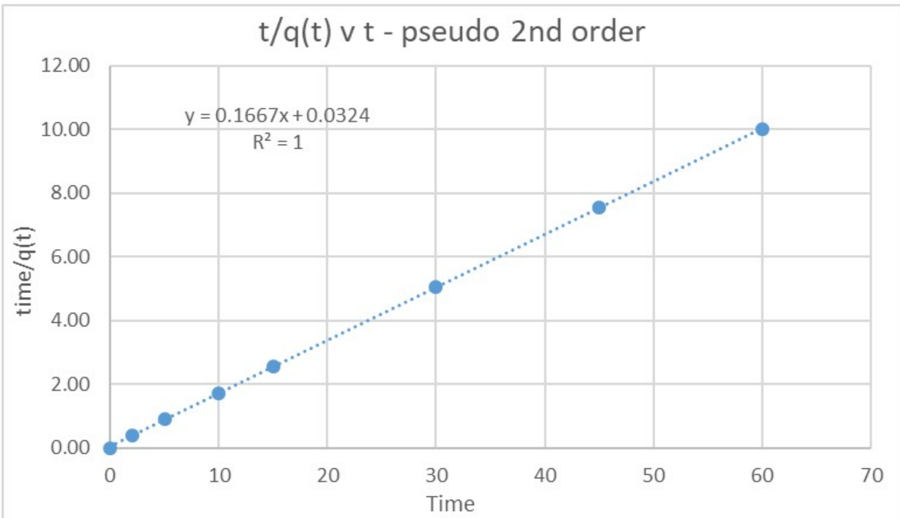

Figure S25: Pseudo second order kinetics for 200 ml of a 10 mg/L with 50 mg MNPs over 1 hour.

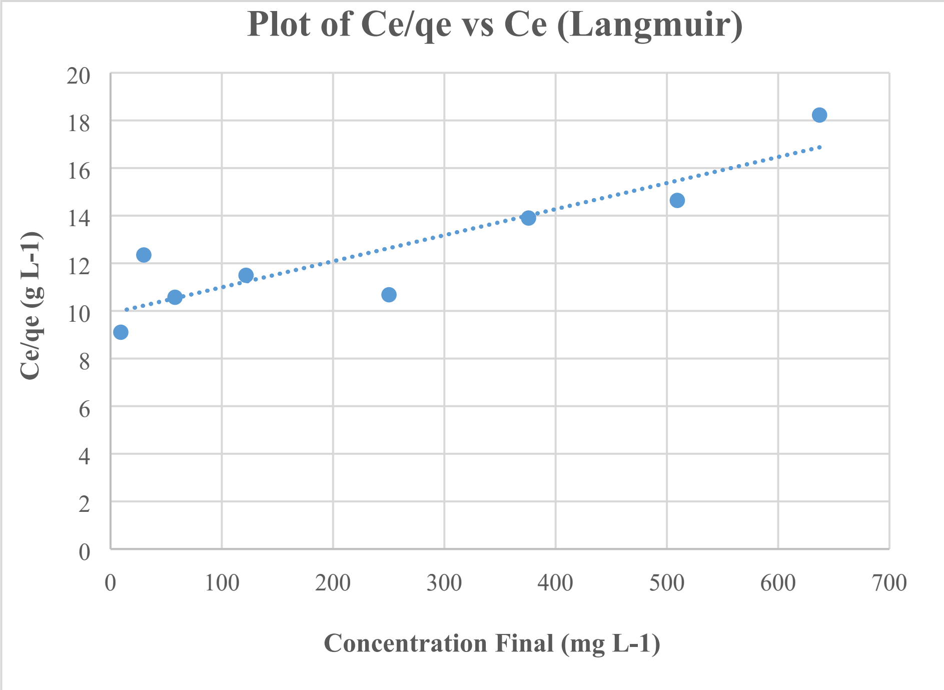

Figure S26: Langmuir isotherm model linear fit.

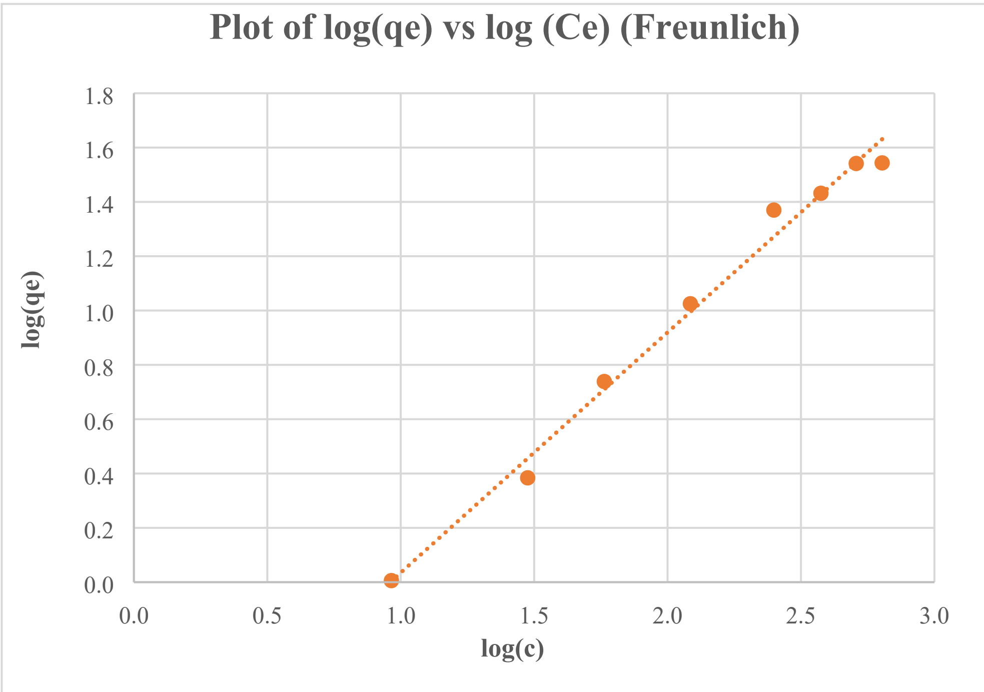

Figure S27: Freundlich Isotherm model linear fit.

Table S2: Raw data used to construct the isotherm.

L	g	M (mol/L)	M (mol/L)
initial vol	**mass NP**	**initial conc (C_i)**	**equi (final) conc (C_e)**
0.1	0.025	0.00172753	0.00170416
0.1	0.025	0.00138555	0.00136228
0.1	0.025	0.00102277	0.00100470
0.1	0.025	0.00068498	0.00066931
0.1	0.025	0.00033277	0.00032569
0.1	0.025	0.00015862	0.00015495
0.1	0.025	0.00008160	0.00007999
0.1	0.025	0.00002535	0.00002467

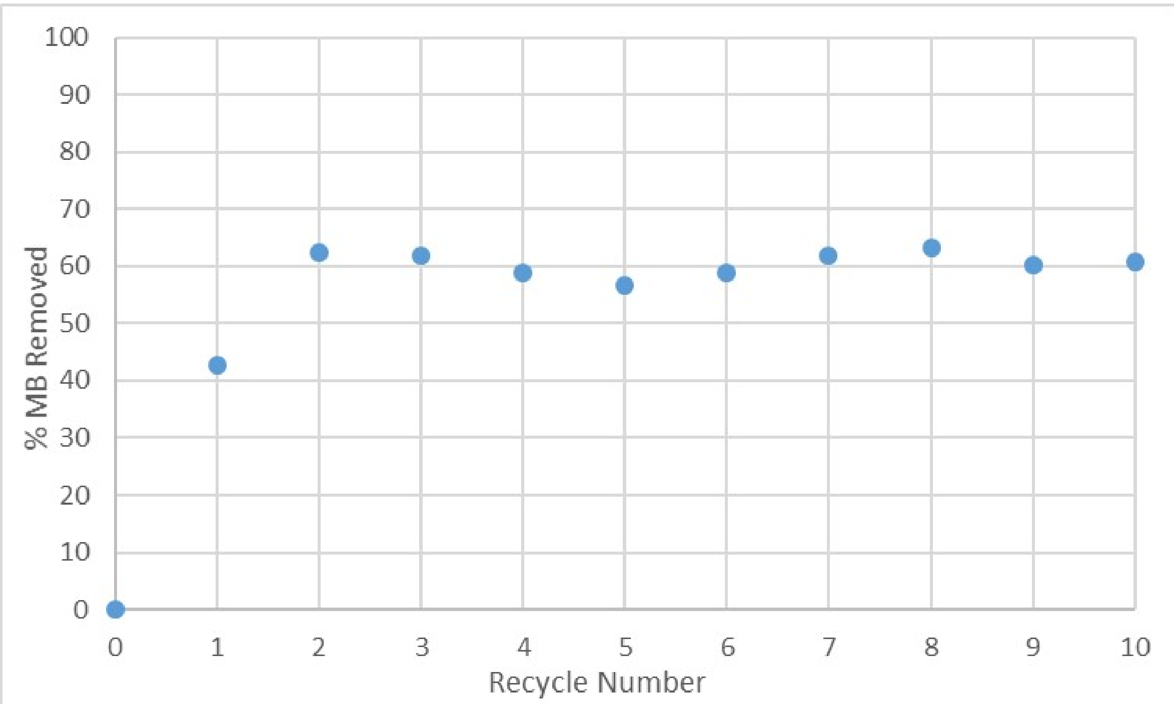

Figure S28: Recycling testing for MNPs.

Results

			Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV):	5.66	**Peak 1:**	5.66	100.0	4.28
Zeta Deviation (mV):	4.28	**Peak 2:**	0.00	0.0	0.00
Conductivity (mS/cm):	0.0176	**Peak 3:**	0.00	0.0	0.00
Result quality	Good				

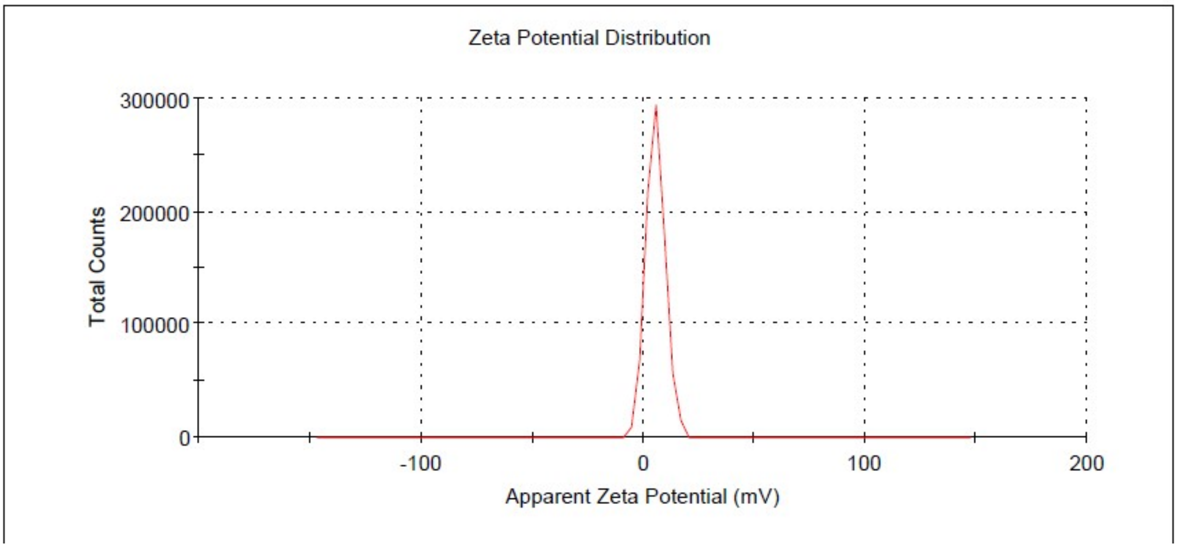

Figure S29: Zeta potential of nanoparticles before any MB extraction.

Results

			Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV):	-6.71	**Peak 1:**	-6.71	100.0	5.97
Zeta Deviation (mV):	5.97	**Peak 2:**	0.00	0.0	0.00
Conductivity (mS/cm):	0.0303	**Peak 3:**	0.00	0.0	0.00
Result quality	Good				

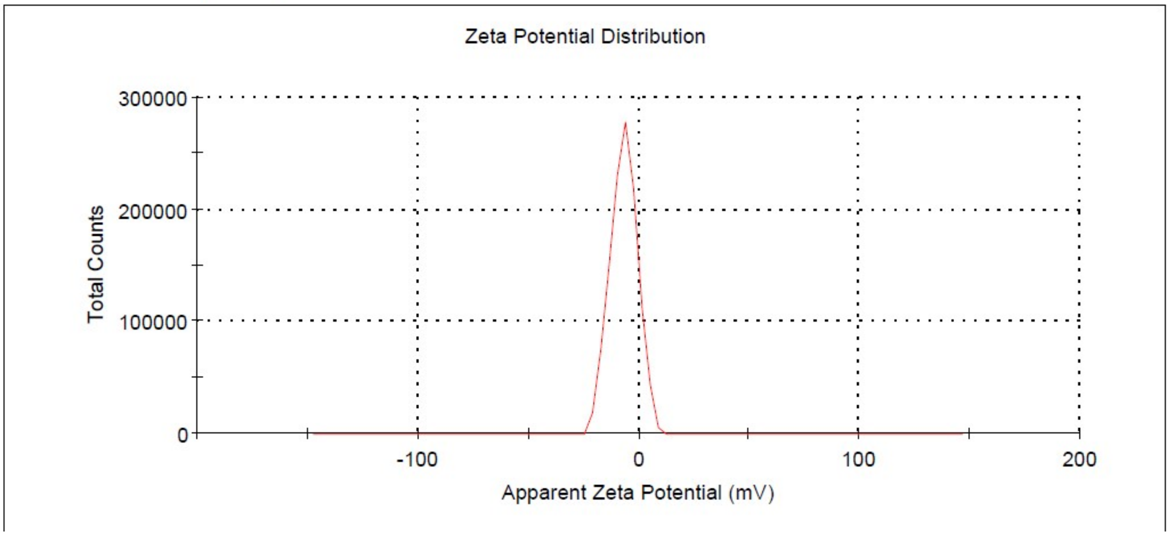

Figure S30: Zeta potential of nanoparticles after any MB extraction.