Modeling of magnetization curves of iron oxide/cerium dioxide reactive sorbents

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AIM: Structural and magnetic characterization and modeling of the hysteresis loops of iron oxide/cerium dioxide sorbents.

Materials preparation

- **Magnetic core –** required amount of ferrous sulphate dissolved in diluted sulphuric acid, addition of equivalent amount of PREFLOC and the concentrated NaOH for precipitation of magnetic iron oxides, the reaction mixture agitated for two additional hours in nitrogen atmosphere, the precipitated iron oxide (presumably magnetite) separated with the aid of permanent magnet and washed several times in deionized water
- **Iron oxide/cerium dioxide sorbent –** precipitated iron oxide re-dispersed in the solution of cerium nitrate, cerium carbonate precipitated with the solution of NH_4HCO_3, composite precursor with **20% of CeO_2** separated with the aid of permanent magnet, washed with deionised water and dried at 110°C
- **Calcination –** the temperature treatments of the **powder** precursor was done in an open porcelain crucible at temperatures ranging **between 473 K and 1173 K** in a muffle furnace

Experimental techniques

- **XRPD (X-Ray Powder Diffraction)** – X'PERT PRO diffractometer by PANALYTICAL, CoKα irradiation (λ = 0.17902 nm), Bragg-Brentano geometry, 2θ range 20° ÷ 110°, evaluation – Rietveld structure refinement method by semi-automatic mode using the High Score Plus program
- **PPMS (Physical Property Measurement System)** – Quantum Design Inc., magnetization curves measured at room (300 K) and low (2 K) temperatures with maximal applied magnetic field ± 4000 kA/m (5 T)

Theoretical models

- **Jiles – Atherton model (isotropic) –** J-A model for simulations of major hysteresis loops of ferro-/ferrimagnetic materials is described by differential equation

$$\frac{\mathrm{d}M}{\mathrm{d}H} = \frac{c\frac{M_S}{a}\left(1-\left(\coth\frac{H_e}{a}\right)^2+\left(\frac{a}{H_e}\right)^2\right)+(1-c)\frac{M_{an}-M}{k\delta(1-c)-\alpha(M_{an}-M)}}{(1-\alpha c)},$$

$$M_{an} = M_s\left(\coth\frac{H_e}{a}-\frac{a}{H_e}\right), \quad H_e = H+\alpha M,$$

where M_{an} is anhysteretic magnetization, H_e is effective magnetic field, M_S is saturation magnetization of material. δ is constant, 1 for increasing field, -1 for decreasing field. Four parameters are fitted by the least squares method:

a – characterizes domain walls density in the magnetic material,
k – determines the hysteresis losses,
α – the mean field parameter representing inter-domain coupling,
c – represents reversible domain wall motion.

- **Langevin model –** used for paramagnetic or superparamagnetic materials, hysteresis loop is simulated by modified Langevin function $L(x) = \coth x - \frac{1}{x}$. We assume spherical shape of particles with diameter *d*, which can be found by fitting method. Magnetization of hysteresis curve is described by

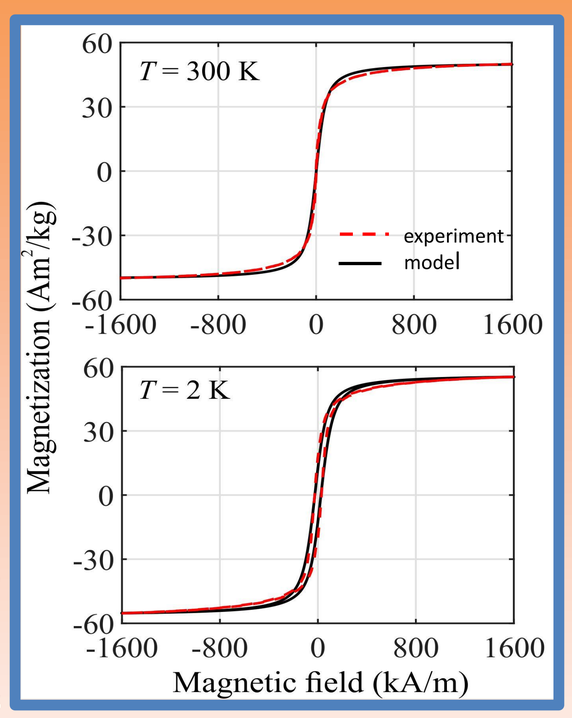
$$M = M_S\, L\left(\frac{\pi\mu_0 M_S H d^3}{6k_B T}\right).$$

The values of J-A and Langevin coefficients are optimized to obtain the root square deviation r^2 (Pearson coefficient) close to 1 showing minimal difference between the experimental and simulated magnetization curves.

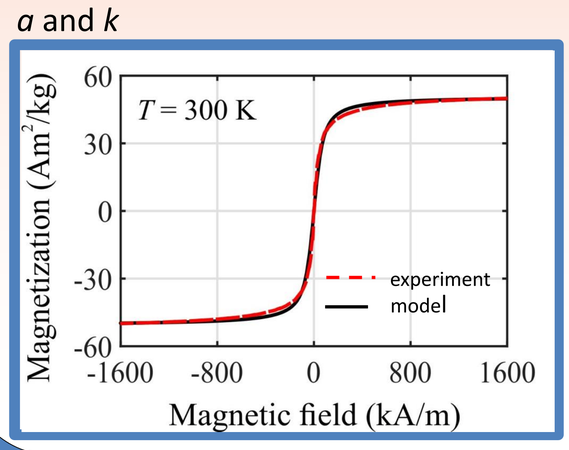
Sorbent calcined at 673 K

Jiles-Atherton (J-A) model

T_{meas} (K)	2	300
H_c (kA/m)	27.51	1.71
M_r (Am²/kg)	18.75	1.78
M_s (Am²/kg)	56.42	50.69
a (kA/m)	33.74	30.11
k (kA/m)	28.12	2.96
α (-)	0.5	0.5
c (-)	0.011	0.004
r^2 (-)	0.999	0.999



- high degradation efficiency against parathion and paraoxon methyl (40% and 72%)
- 20.1% of CeO_2, 15.3% of Fe_3O_4 and 64.6 % of γ-Fe_2O_3 with the crystallite sizes 6.63 nm, 7.89 nm, and 15.54 nm
- simulated loops sensitive to parameters *a* and *k*



Langevin model

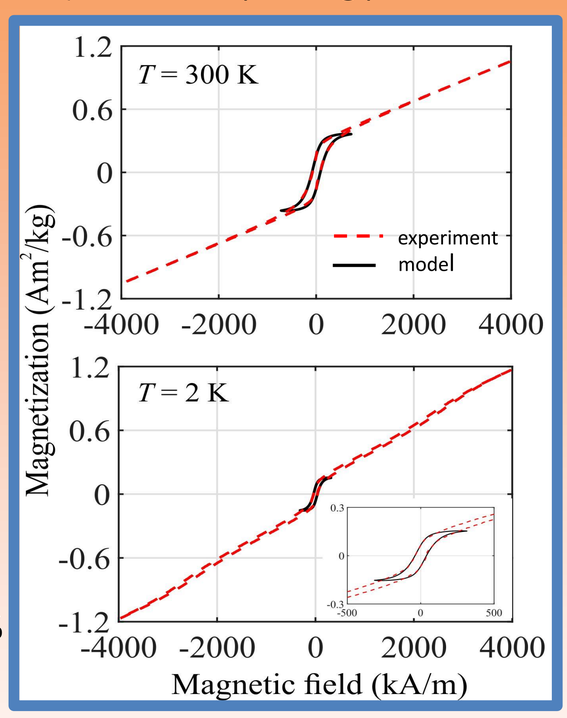
- comparison to Langevin function due to almost superparamagnetic state of the sorbent
- estimated diameter of particles *d* = 160.5 nm with r^2 = 0.999
- well agreement with the Nanozetasizer measurement: $d \approx 140$ nm

Sorbent calcined at 1073 K

Jiles-Atherton (J-A) model

Experimental magnetization curves (dashed red lines) and their parameters compared to the J-A model (black solid lines) with corresponding parameters:

T_{meas} (K)	2	300
H_c (kA/m)	39.12	78.15
M_r (Am²/kg)	0.06	0.16
M_s (Am²/kg)	0.17	0.41
a (kA/m)	24.47	53.67
k (kA/m)	51.85	106.04
α (-)	0.5	0.5
c (-)	0.1	0.1
r^2 (-)	0.997	0.996



- lower degradation efficiency against parathion and paraoxon methyl (5% and 36%)
- crystallite size and amount of CeO_2 obtained from XRD: 28.94 nm and 20.7%
- iron oxides completely transformed to hematite (93.36 nm, 79.3%)
- at higher magnetic fields, linear dependence of magnetization indicates anti-ferromagnetic behaviour of hematite, while at lower fields typical ferromagnetic reversal with high H_c and low M_s (see Table) is observed
- increase of *a*, *k*, and *c* parameters in comparison to 637 K calcined sorbent refers to growth of energetic losses and reversible component of magnetization
- cooling below 263 K (Morin transition) should lead to suppression of spin canting, nevertheless measured loop at 2 K still exhibits ferromagnetic contribution with lower H_c and M_s than at 300 K (decrease of parameters *a* and *k*)

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