"Gheorghe Asachi" Technical University of Iasi, Romania
Faculty of Chemical Engineering and Environmental Protection

MAGNETIC CHITOSAN COMPOSITE PARTICLES: SYNTHESIS REPRODUCIBILITY AND PARAMETER STUDY

Doina Hritcu, Maria C. Alexandrica,
Alina Ibanescu, Marcel I. Popa

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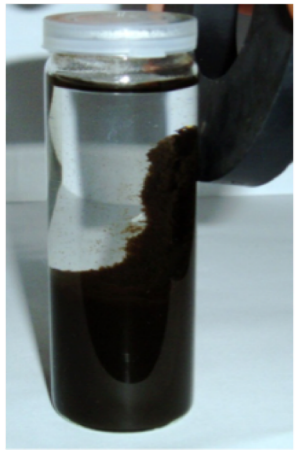
Introduction/motivation

Magnetic adsorbents → Facile separation → **Lower cost**



Magnetic chitosan composites

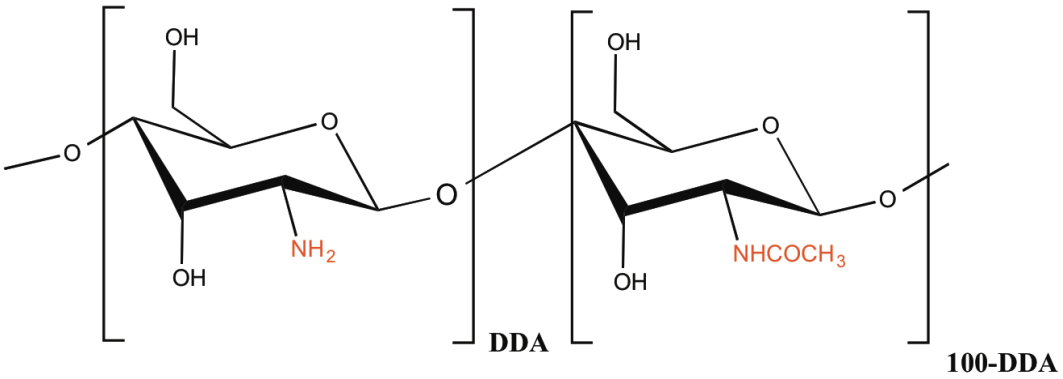
- environmentally friendly
- sustainable raw material
- abundant functional groups

Project goal

- **Potential problem**: variability of the natural raw material
- **Proposed strategy**: evaluate influence and find ways to overcome it

Lot to lot variability in chitosan **structure:**

- Degree of deacetylation
- Molecular weight distribution
- Copolymer block sequence
- Block lengths

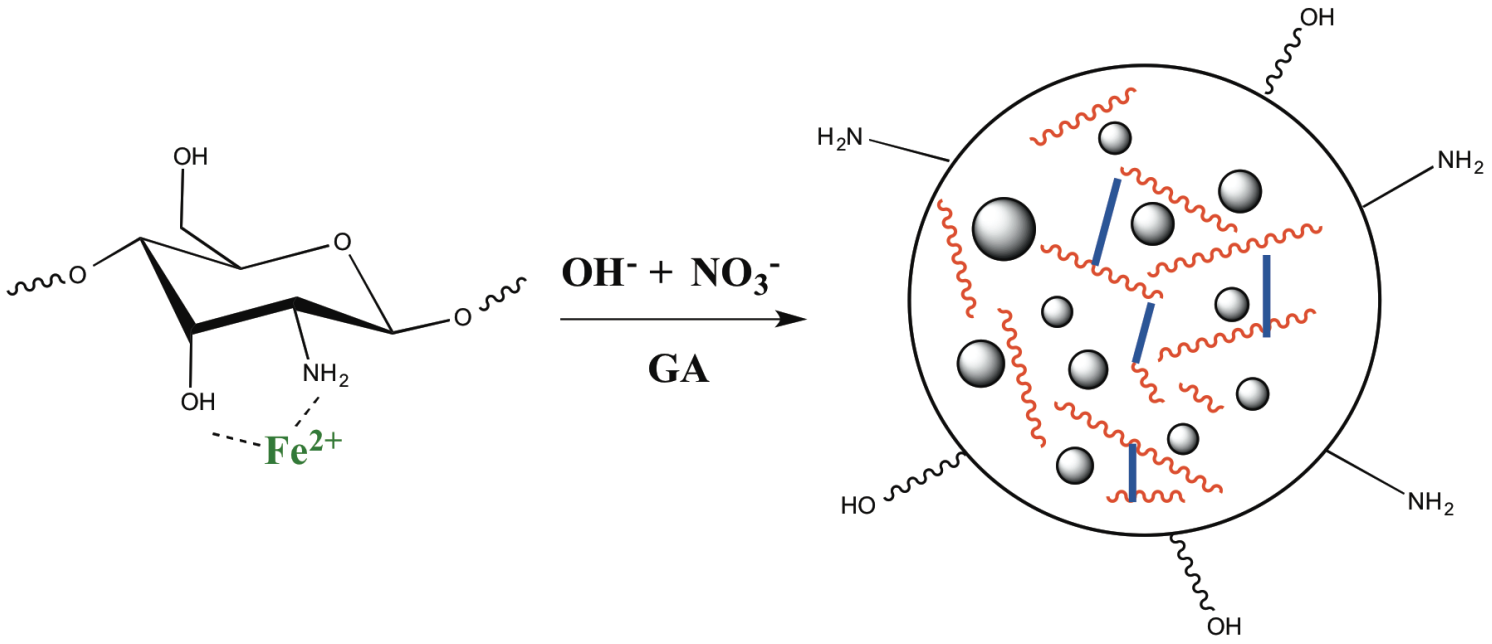


Variability in **properties**:

- Solubility
- Viscosity
- Availability of reactive groups

Synthesis

1. CS in acetic acid solution + ferrous chloride
2. Ammonium solution added gradually -> CS precipitation
3. Partial oxidation of ferrous ions -> Magnetite
4. Crosslinking with glutaraldehyde
5. Acid/base treatment; colloidal stabilization



$$12Fe(OH)_2 + NO_3^- \rightarrow 4Fe_3O_4 + NH_3 + 10H_2O + HO^-$$

Synthesis parameter study

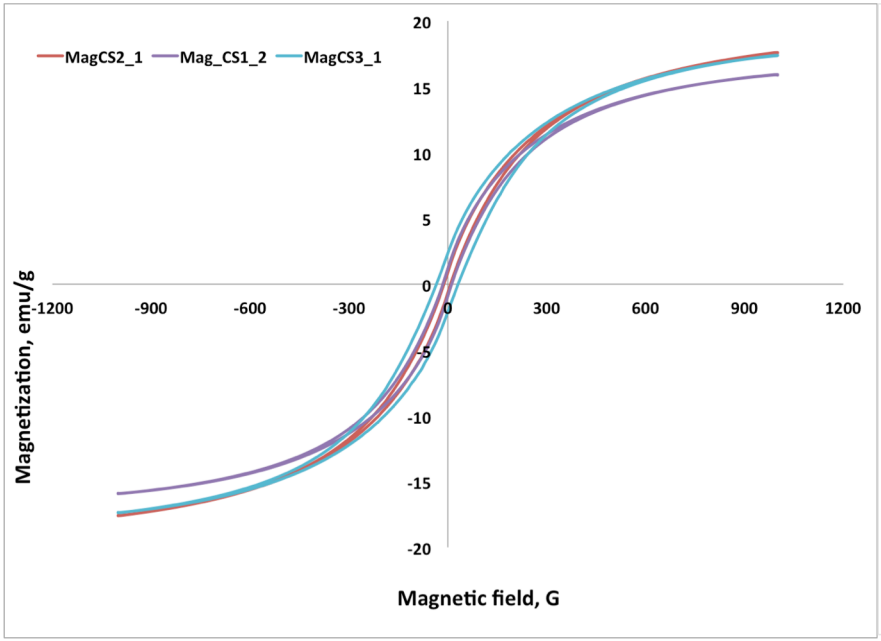
1. **INPUT PARAMETERS:**
    1. CS properties:

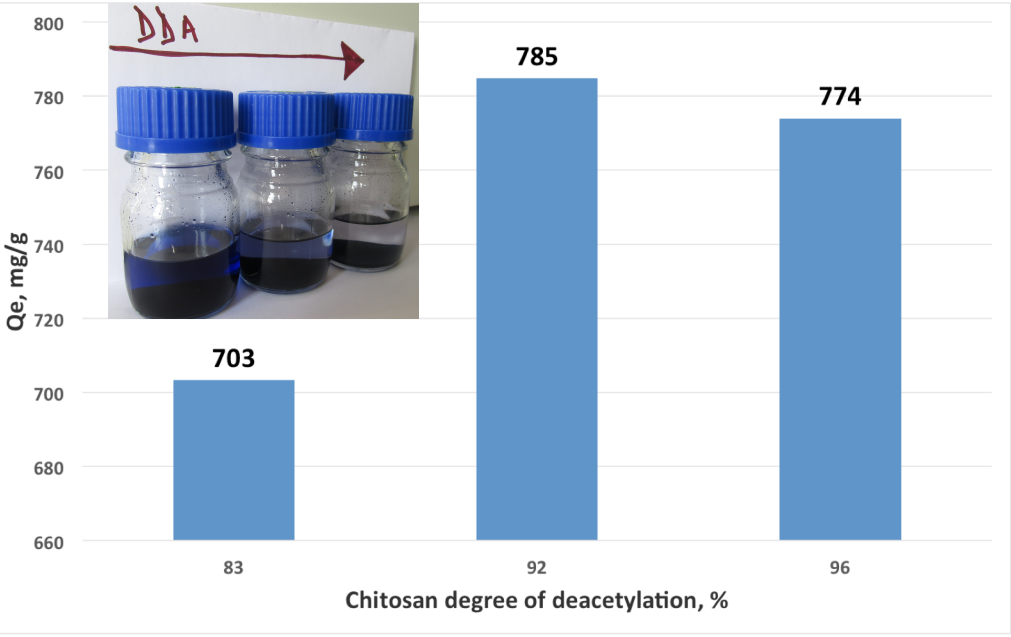
    CS low molecular weight specifications
        1. Viscosity of 1% solution in 1% acetic acid 20-300cPs
        2. DDA>75%
    2. Ferrous chloride amount
    3. Ammonia concentration
    4. Glutaraldehyde concentration

2. **OUTPUT PARAMETERS (PRODUCT CHARACTERIZATION):**
    1. Adsorption capacity
    2. Saturation magnetization
    3. Average particle size
    4. Yield

1. CHITOSAN PROPERTIES

Batch	CS DDA, %	CS viscosity, CPS	Particle size Dv/Dn, µm/µm	Yied, %
MagCS3_1	83	53	169/46	72
MagCS1_2	92.2	42	191/73	99
MagCS2_1	96.1	35	148/43	93



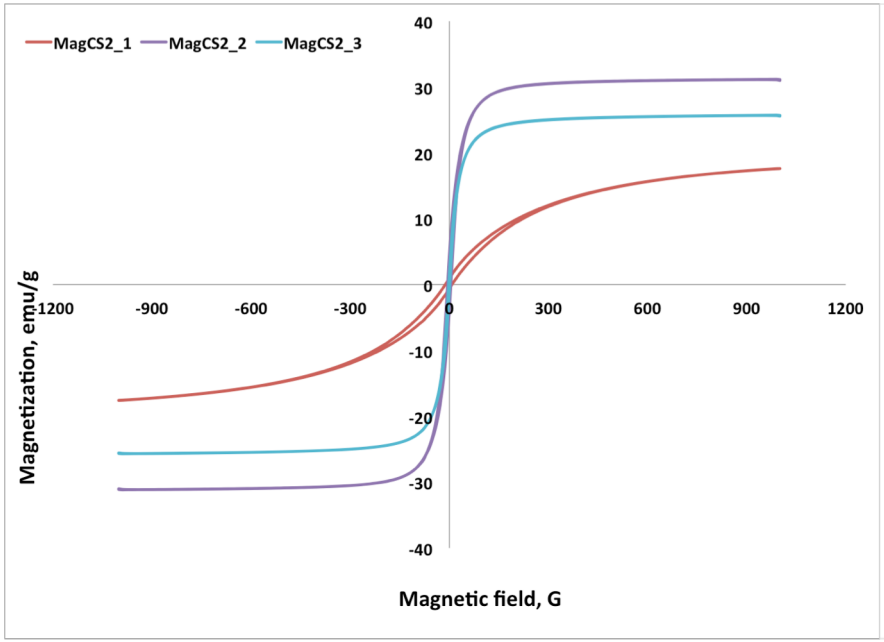


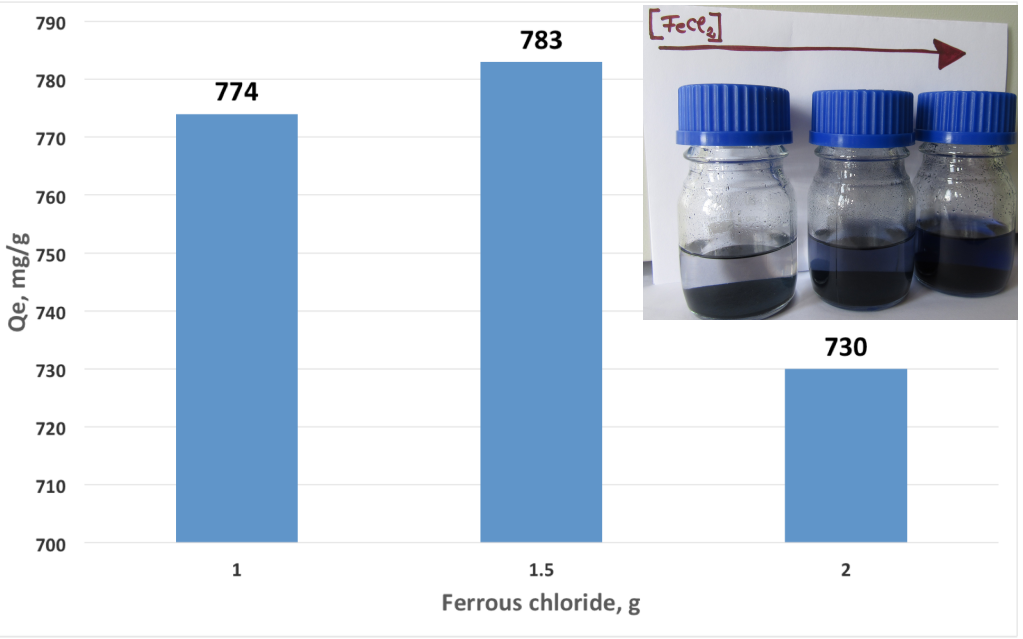
Dye adsorption by electrostatic attraction

MCC-NH_3^+---SO_3^--Dye

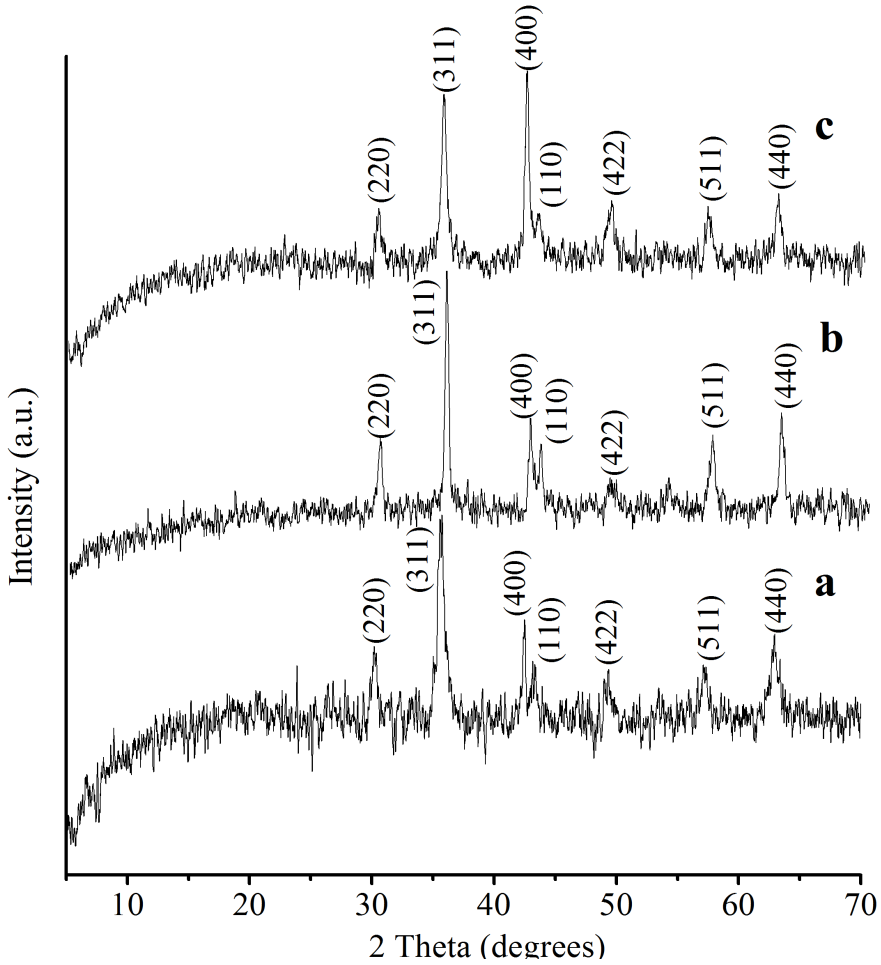
2. FERROUS CHLORIDE AMOUNT

Batch	$FeCl_2.4H_2O$ g	$[NH_3]$ M	[GA] %	Particle size Dv/Dn, µm/µm	Yied, %
MagCS2_1	1	0.5	5	148/43	96
MagCS2_3	1.5	0.5	5	119/55	75
MagCS2_2	2	0.5	5	268/186	82





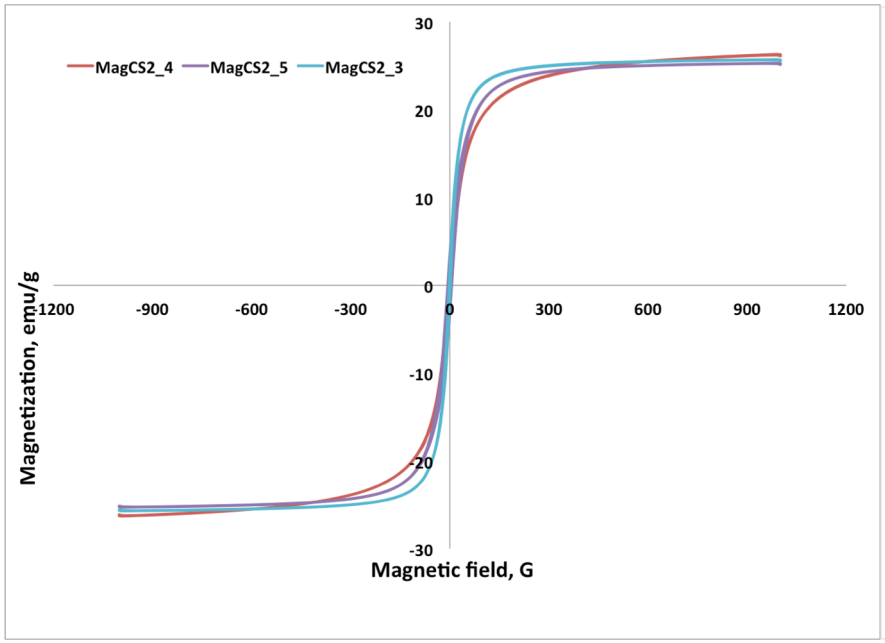
XRD analysis

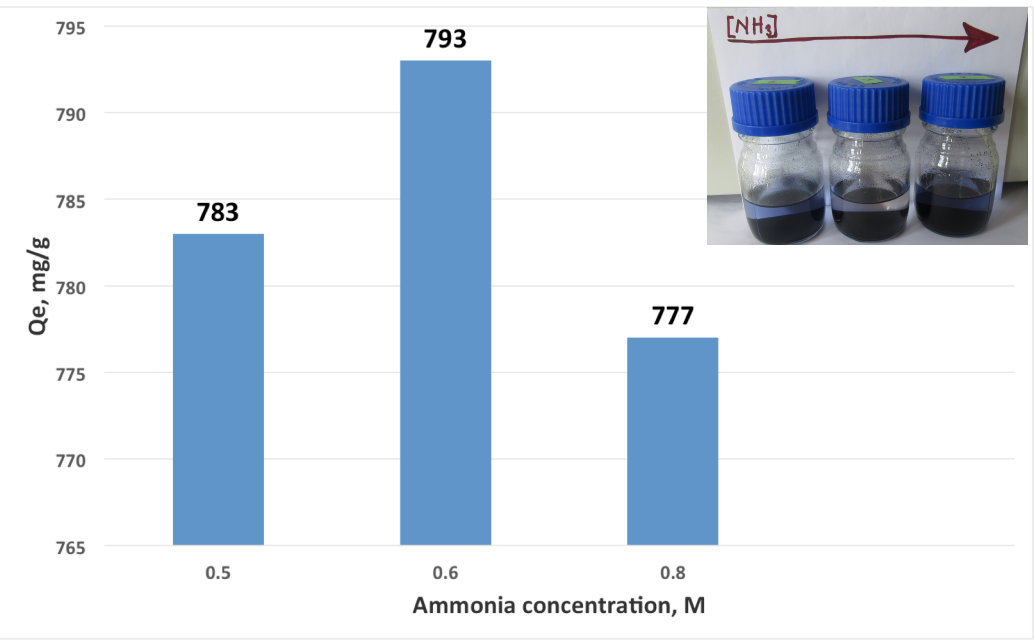


Symbol	$FeCl_2.4H_2O$ g	Crystallite size nm
(a)	1	9.8
(c)	1.5	12.6
(b)	2	22.6

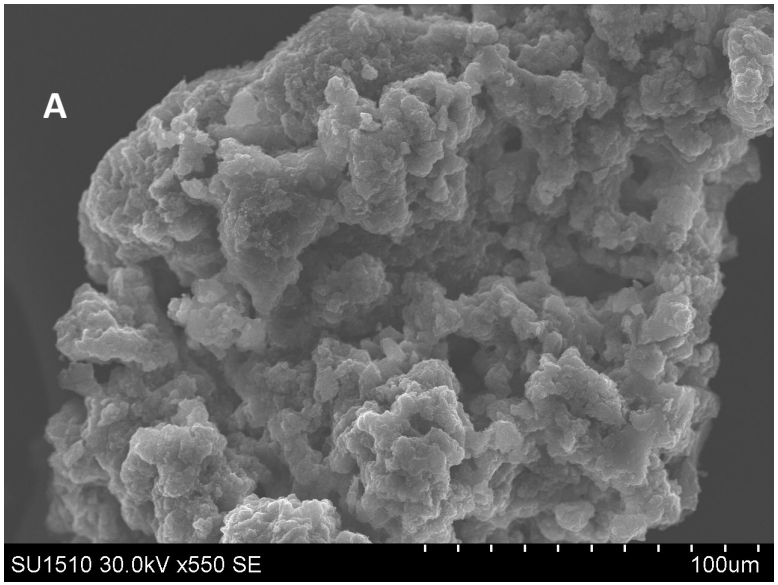
3. AMMONIA CONCENTRATION

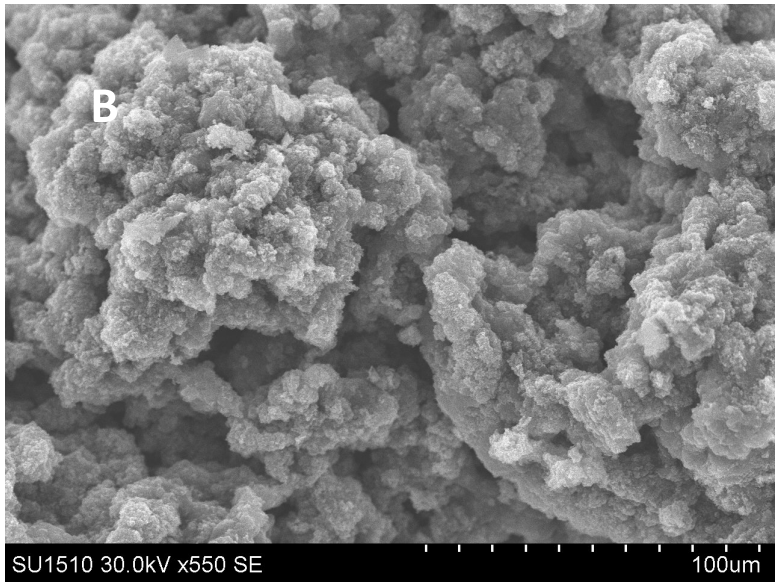
Batch	$FeCl_2.4H_2O$ g	$[NH_3]$ M	[GA] %	Particle size Dv/Dn, µm/µm	Yied, %
MagCS2_3	1.5	0.5	5	119/55	75
MagCS2_4	1.5	0.6	5	193/77	82
MagCS2_5	1.5	0.8	5	239/146	89





Comparative morphology





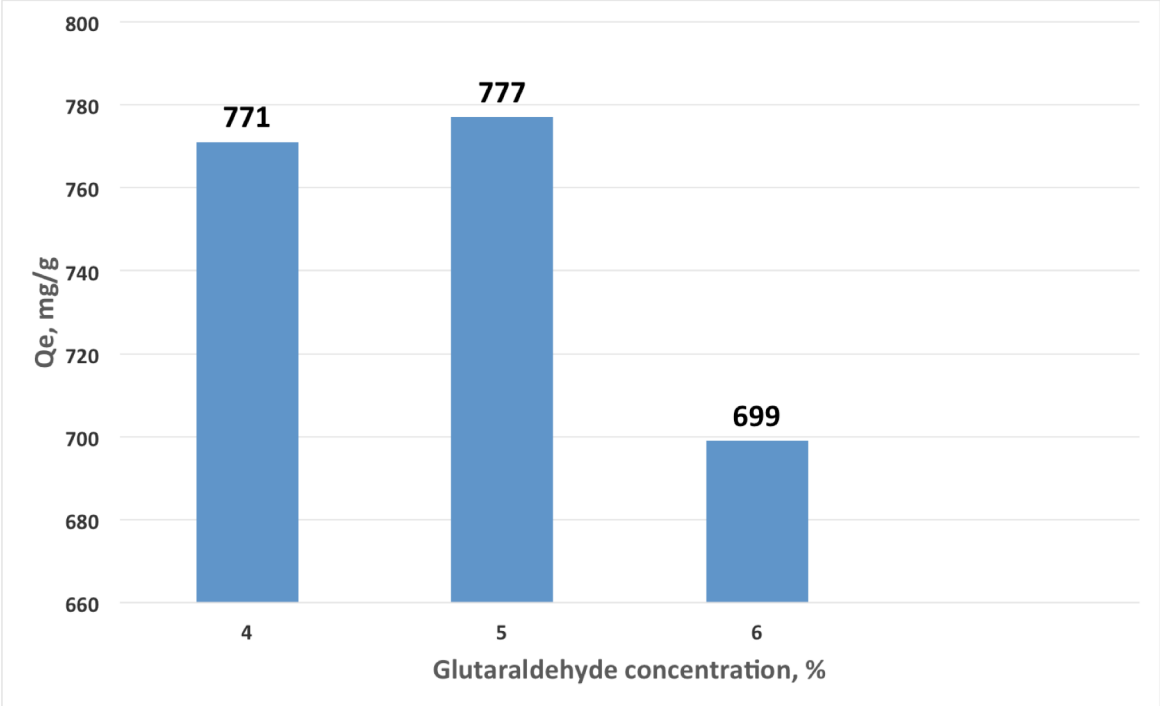
MagCS2_1
(initial recipe)

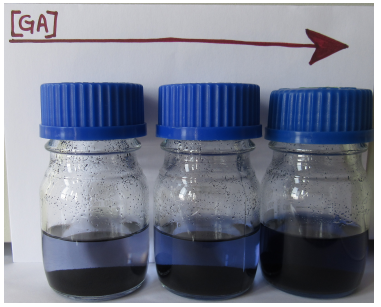
MagCS2_5
(recipe with higher magnetization)

Batch	$FeCl_2.4H_2O$ g	$[NH_3]$ M	[GA] %	Magnetization, emu/g	Particle size Dv/Dn, µm/µm	Qe RB19 mg/g
MagCS2_1	1	0.5	5	17.6	119/55	774
MagCS2_5	1.5	0.8	5	26.1	193/77	777

4. GLUTARALDEHYDE CONCENTRATION

Batch	$FeCl_2.4H_2O$ g	$[NH_3]$ M	[GA] %	Magnetization, emu/g	Particle size Dv/Dn, µm/µm	Yied, %
MagCS2_7	1.5	0.8	4		119/55	92
MagCS2_5	1.5	0.8	5	26.1	193/77	89
MagCS2_6	1.5	0.8	6		239/146	96





Reproducibility and scale-up

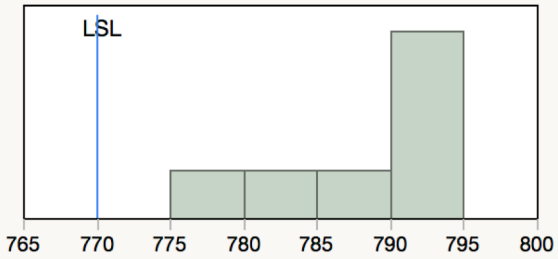
Batch	$FeCl_2.4H_2O$ g	$[NH_3]$ M	[GA] %	Magnetization, emu/g	Dv/Dn, µm/µm	Yied, %	Qe RB19 mg/g
MagCS3_2	1.5	0.6	4	**23.9**	119/55	88	**781.1**
MagCS1_3	1.5	0.6	5	**23.2**	193/77	82	**777.3**
MagCS2_4	1.5	0.6	5	**26.1**	239/146	82	**793.0**
MagCS2_9	1.5x2	0.6	5	**22.0**	296/223	85	**786.8**
MagCS2_10	1.5x2	0.6	5	**21.4**	289/209	88	**793.9**
MagCS2_11	1.5x2	0.6	5	**24.8**	301/230	88	**791.9**
MagCS2_12	1.5x2	0.6	4 (New lot)	**21.3**	270/181	88	**791.9**

- Three lots of chitosan
- Small scale versus large scale
- New lot of GA

Specifications and process capability

Distributions

Qe RB19, mg/g



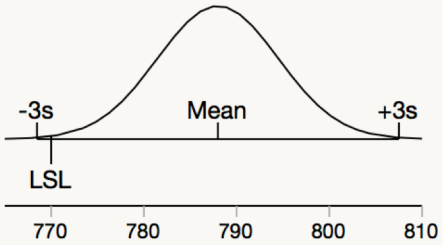
Summary Statistics

Mean	787.98571
Std Dev	6.5034423
N	7
Minimum	777.3
Maximum	793.9

Capability Analysis

Specification	Value	Portion	% Actual
Lower Spec Limit	770	Below LSL	0.0000
Spec Target	.	Above USL	.
Upper Spec Limit	.	Total Outside	0.0000

Long Term Sigma



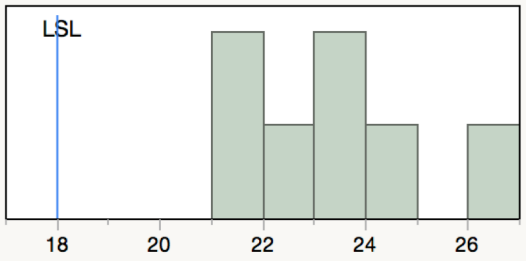
Sigma = 6.50344

Capability	Index	Lower CI	Upper CI
CP	.	.	.
CPK	0.922	0.353	1.481
CPM	.	.	.
CPL	0.922	0.353	1.481
CPU	.	.	.

Portion	Percent	PPM	Sigma Quality
Below LSL	0.2841	2841.1847	4.266
Above USL	.	.	.
Total Outside	0.2841	2841.1847	4.266

Qe>770 mg/g

Magnetization, emu/g



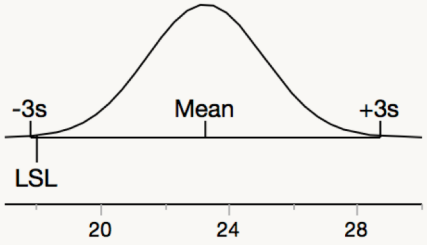
Summary Statistics

Mean	23.25
Std Dev	1.8160488
N	7
Minimum	21.34
Maximum	26.14

Capability Analysis

Specification	Value	Portion	% Actual
Lower Spec Limit	18	Below LSL	0.0000
Spec Target	.	Above USL	.
Upper Spec Limit	.	Total Outside	0.0000

Long Term Sigma



Sigma = 1.81605

Capability	Index	Lower CI	Upper CI
CP	.	.	.
CPK	0.964	0.374	1.544
CPM	.	.	.
CPL	0.964	0.374	1.544
CPU	.	.	.

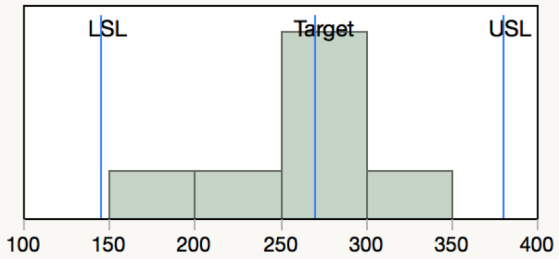
Portion	Percent	PPM	Sigma Quality
Below LSL	0.1921	1920.7540	4.391
Above USL	.	.	.
Total Outside	0.1921	1920.7540	4.391

Magn>18 emu/g

Specifications and process capability

Distributions

Dv, um



145 μm<Dv<380 μm

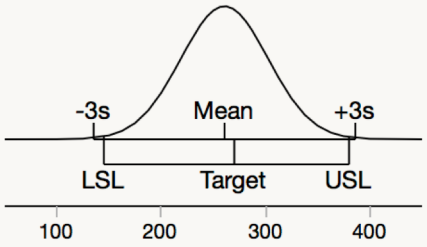
Summary Statistics

Mean	260.6
Std Dev	41.807455
N	7
Minimum	193
Maximum	301

Capability Analysis

Specification	Value	Portion	% Actual
Lower Spec Limit	145	Below LSL	0.0000
Spec Target	270	Above USL	0.0000
Upper Spec Limit	380	Total Outside	0.0000

Long Term Sigma

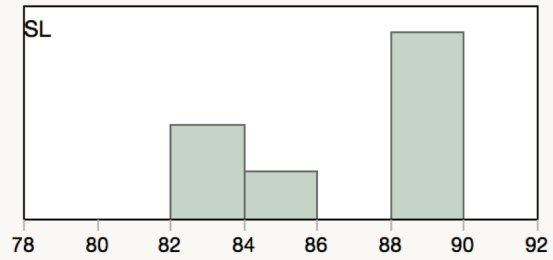


Sigma = 41.8075

Capability	Index	Lower CI	Upper CI
CP	0.937	0.425	1.454
CPK	0.922	0.345	1.499
CPM	0.856	.	.
CPL	0.922	0.353	1.481
CPU	0.952	0.368	1.526

Portion	Percent	PPM	Sigma Quality
Below LSL	0.2846	2845.6420	4.265
Above USL	0.2145	2145.4139	4.356
Total Outside	0.4991	4991.0559	4.076

Yield, %



Yield>78%

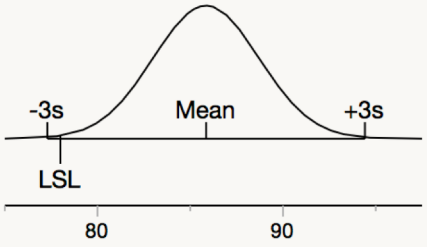
Summary Statistics

Mean	85.857143
Std Dev	2.8535692
N	7
Minimum	82
Maximum	88

Capability Analysis

Specification	Value	Portion	% Actual
Lower Spec Limit	78	Below LSL	0.0000
Spec Target	.	Above USL	.
Upper Spec Limit	.	Total Outside	0.0000

Long Term Sigma

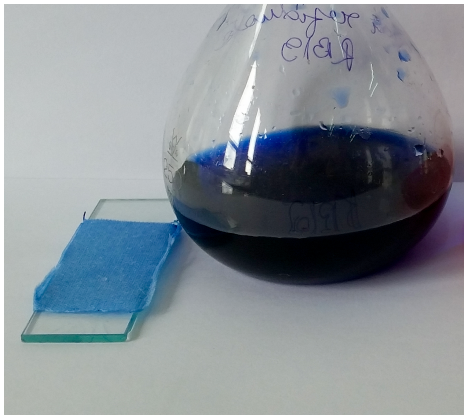


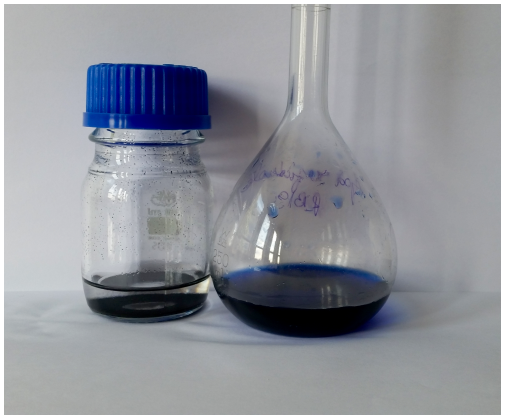
Sigma = 2.85357

Capability	Index	Lower CI	Upper CI
CP	.	.	.
CPK	0.918	0.351	1.475
CPM	.	.	.
CPL	0.918	0.351	1.475
CPU	.	.	.

Portion	Percent	PPM	Sigma Quality
Below LSL	0.2949	2948.5933	4.253
Above USL	.	.	.
Total Outside	0.2949	2948.5933	4.253

Product testing





Waste water from cotton dyeing (1g/L RB19, 1g/L NaCl, 1g/L Na_2CO_3, pH=6.4)

Batch	Ci mg/ml	Cf mg/ml	Volume ml	Sorbent mg	pH	Qe mg/g
MagCS2_9	0.637	0.001	25	22	2.2	709

Conclusions

- The synthesis procedure is robust with respect to chitosan variability within the investigated range
- Lower degree of deacetylation in chitosan may be compensated by decreasing the crosslink level
- Magnetization may be increased by using more iron salt, without affecting the purity of the magnetite component
- A scaled-up reproducible procedure was developed and validated
- Quality control and product specifications:
  - Qe (RB19)>770mg/g
  - Magnetization > 18 emu/g
  - Dv = 145 – 380 μm
  - Yield > 78%
- Process capability was verified
- The use of the adsorbent for waste water treatment was demonstrated

Acknowledgements

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Project title:
“GREEN” MAGNETIC ADSORBENT FOR WASTEWATER TREATMENT: MODE OF SYNTHESIS AND USE (GreenMagAds)

Mihaela Silion

THANK YOU FOR YOUR ATTENTION!