Objectives and activities - Stage I-2017

O_1. Investigate composite particles structure-property relationship;

1.1. Produce three lots of composite particles with three lots of chitosan using the already developed small scale procedure

1.2. Investigate the influence of the raw material (chitosan) characteristics upon the composite particle properties

O2. Optimize small scale technology for composite particle synthesis;

2.1. Identify the changes in synthesis parameters that compensate for chitosan variability

2.2. Elaborate an experimental model that relates raw material and product properties using design of experiment methodology and statistical analysis; verify model hypotheses

O_3. Scale-up adsorbent synthesis procedure

3.1. Pilot-scale parameter study (stirring rate, addition rate, temperature, solution concentration)

3.2. Propose and optimize a cost-effective cleaning procedure

3.3. Particle characterization (size, magnetization, concentration of surface functional groups)

3.4. Reproducibility study

Results and conclusions

The parameter study followed the following variables:

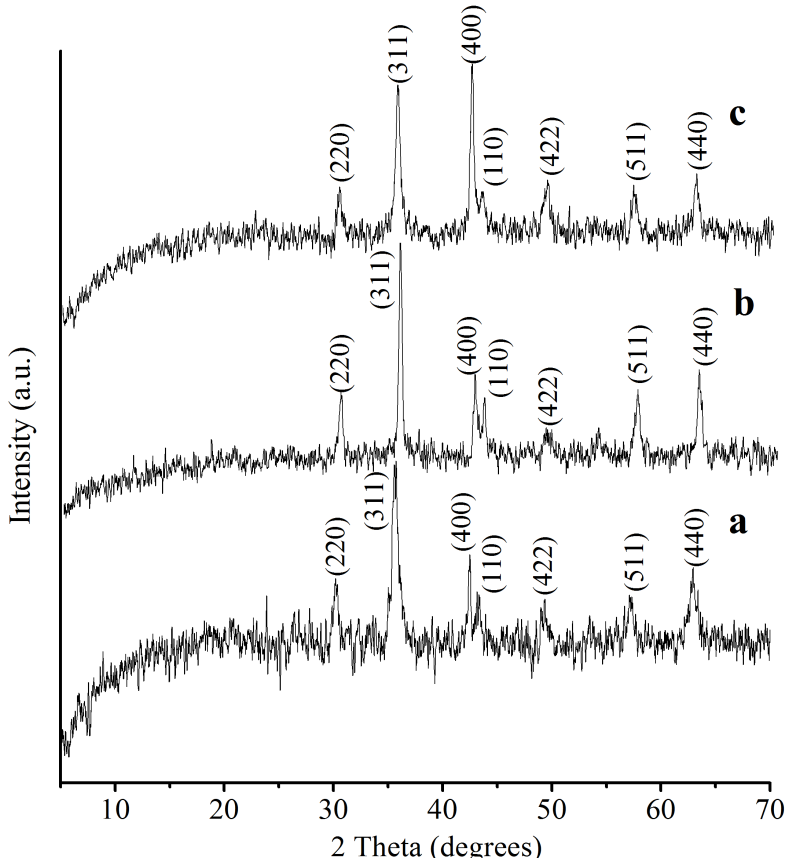
1. Input variables
    a. Chitosan properties (deacetilation degree, solution viscosity)
    b. Iron chloride amount
    c. Ammonia concentration
    d. Glutaraldehyde concentration
2. Output parameters
    a. Adsorption capacity for RB19 anionic dye
    b. Saturation magnetization
    c. Average particle diameter
    d. Synthesis yield

Influence of chitosan properties:

Batch	CS DDA, %	CS viscosity, CPS	Yied, %	Magnetization, emu/g	Particle size Dv/Dn, µm/µm	Qe RB19, mg/g
MagCS3_1	83	53	72	17.4	169/46	703
MagCS1_2	92.2	42	99	15.9	191/73	785
MagCS2_1	96.1	35	93	17.6	148/43	774

Influence of the iron chloride amount:

Batch	$FeCl_2.4H_2O$ g	$[NH_3]$ M	[GA] %	Magnetization, emu/g	Particle size Dv/Dn, µm/µm	Yied, %	Qe RB19, mg/g
MagCS2_1	1	0.5	5	17.6	148/43	96	774
MagCS2_3	1.5	0.5	5	25.6	119/55	75	783
MagCS2_2	2	0.5	5	31.0	268/186	82	730



Influence of the ammonia concentration:

Batch	$FeCl_2.4H_2O$ g	$[NH_3]$ M	[GA] %	Magnetization, emu/g	Particle size Dv/Dn, µm/µm	Yied, %	Qe RB19, mg/g
MagCS2_3	1.5	0.5	5	25.6	119/55	75	783
MagCS2_4	1.5	0.6	5	26.1	193/77	82	793
MagCS2_5	1.5	0.8	5	25.2	239/146	89	777

Influence of glutaraldehyde concentration:

Batch	$FeCl_2.4H_2O$ g	$[NH_3]$ M	[GA] %	Magnetization, emu/g	Particle size Dv/Dn, µm/µm	Yied, %	Qe RB19, mg/g
MagCS2_7	1.5	0.8	4		254/173	92	771
MagCS2_5	1.5	0.8	5	25.2	239/146	89	777
MagCS2_6	1.5	0.8	6		244/152	96	699

Reproducibility study after optimization:

Batch	$FeCl_2.4H_2O$ g	$[NH_3]$ M	[GA] %	Yied, %	Magnetization, emu/g	Particle size Dv/Dn, µm/µm	Qe^2 RB19, mg/g
MagCS3_2	1.5	0.6	4	88	23.9	215/98	781
MagCS1_3	1.5	0.6	5	82	23.2	259/181	777
MagCS2_4	1.5	0.6	5	82	26.1	193/77	793

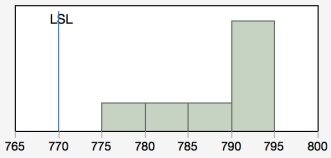
Pilot scale results:

Batch	$FeCl_2.4H_2O$ g	$[NH_3]$ M	[GA] %	Yied, %	Magnetization, emu/g	Particle size Dv/Dn, µm/µm	Qe^2 RB19, mg/g
MagCS2_9	1.5x2	0.6	5	85.0	22.0	296/223	786.8
MagCS2_10	1.5x2	0.6	5	88.1	21.4	289/209	793.9
MagCS2_11	1.5x2	0.6	5	88.4	24.8	301/230	791.9
MagCS2_8	1.5x2	0.6	5 (New lot)	72.3	23.4	292/216	681.9
MagCS2_12	1.5x2	0.6	4 (New lot)	88.3	21.3	270/181	791.9

Statistical analysis for proposing product specification:

Distributions

Qe RB19, mg/g



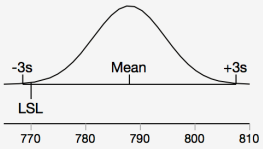
Summary Statistics

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

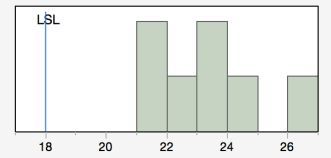


Sigma = 6.50344

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

Magnetization, emu/g



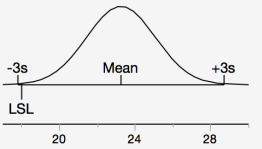
Summary Statistics

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



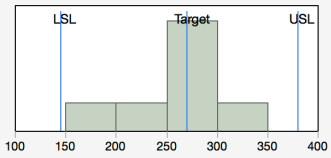
Sigma = 1.81605

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

Distributions

Dv, um



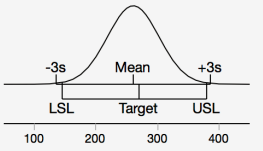
Summary Statistics

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

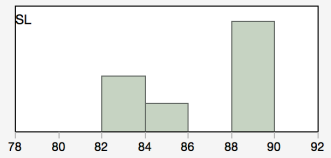


Sigma = 41.8075

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, %



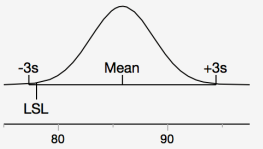
Summary Statistics

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

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
- A simple cleaning procedure was developed
- Quality control and product specifications:
    - Qe (RB19)>770mg/g
    - Magnetization > 18 emu/g
    - Dv = 145 – 380 mm
    - Yield > 78%
- Process capability was verified