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

Process development for reproducible synthesis of magnetic eco-friendly adsorbent

Doina Hritcu, Alina Ibanescu, Marcel I. Popa

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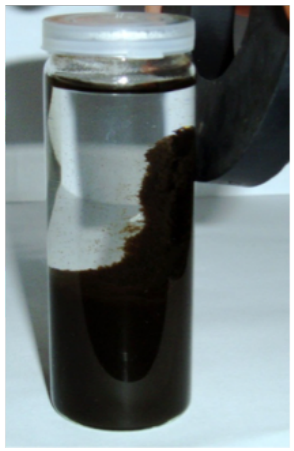
Introduction/motivation

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



Magnetic chitosan composites

- environmentally friendly
- sustainable raw material
- abundant functional groups

- Magnetite/chitosan composite developed in previous project
- Iron oxide particles encapsulated upon formation
- Composite particles produced in one step
- Magnetic material/matrix ratio may be tuned to application
- Superior adsorption properties demonstrated

Chitosan-encapsulated magnetic particles produced by in situ oxidation of ferrous ions	**Ion**	**Qe (mg/g)**
	Th (IV)	313
	UO_2 (II)	667
	Co (II)	588
	Ni (II)	833
	Cu (II)	234

Polymer Bulletin, 67(1), 177-186 (2011)
Carbohydr. Polym. 2012; 87, 1185–1191

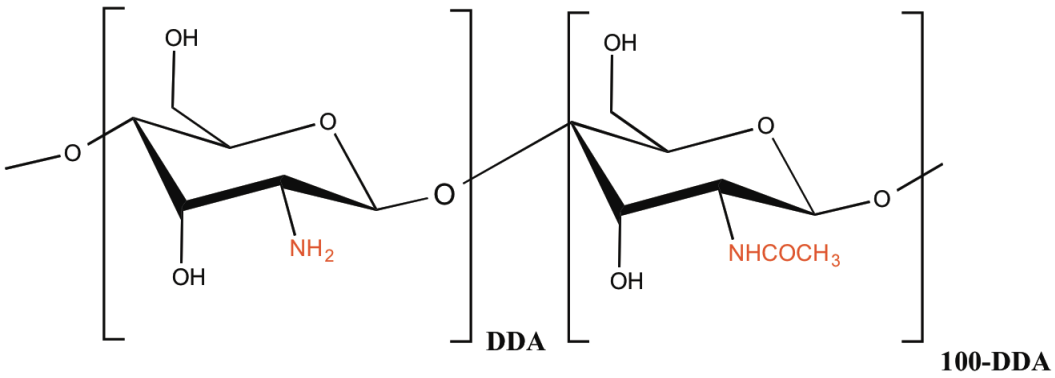
Int. Rev. Chem. Eng. 2012, 4, 364–368
Chem. Eng. J. 2012, 203, 130–141

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

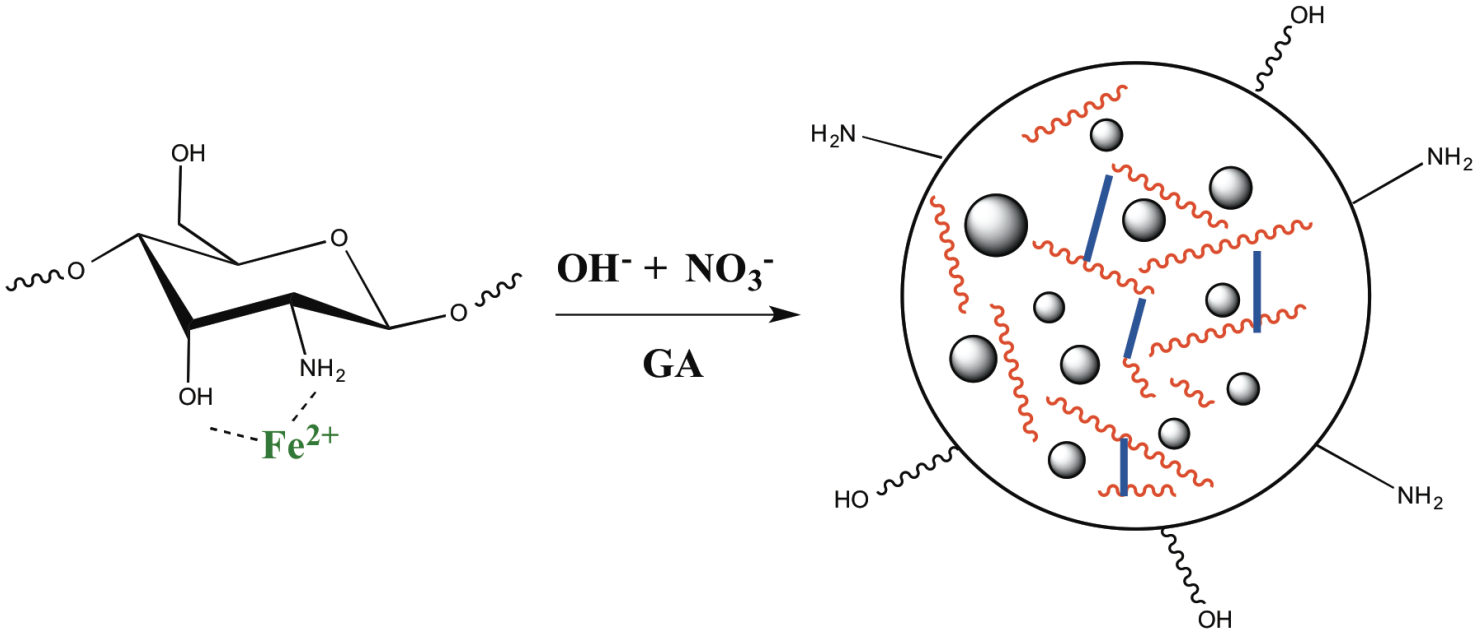


Variability in **properties**:

- 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:

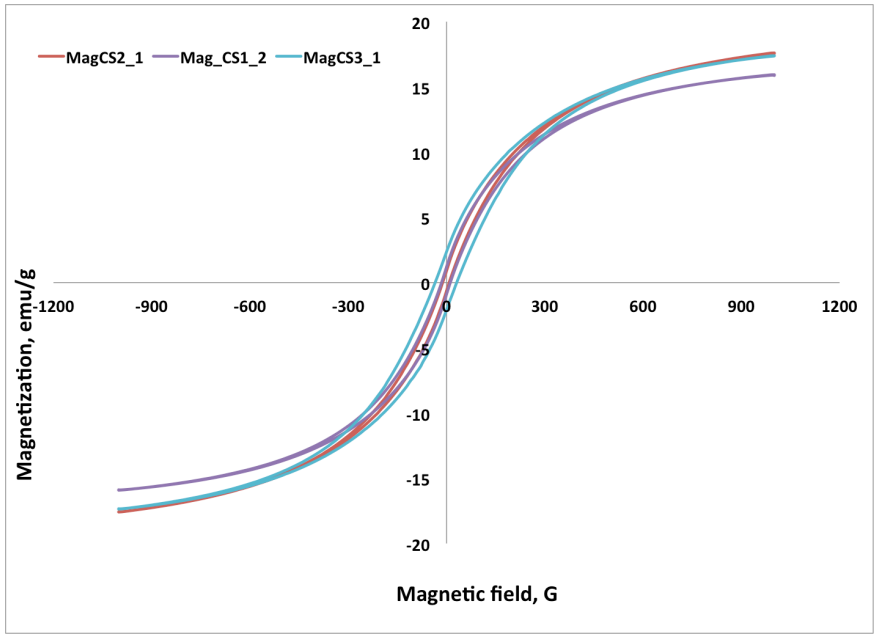
    CS low molecular weight specifications
        1. Viscosity of 1% solution in 1% acetic acid 20-300cPs
        2. DDA>75%
    2. Ferrous chloride amount
    3. Ammonia concentration
    4. Glutaraldehyde concentration

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

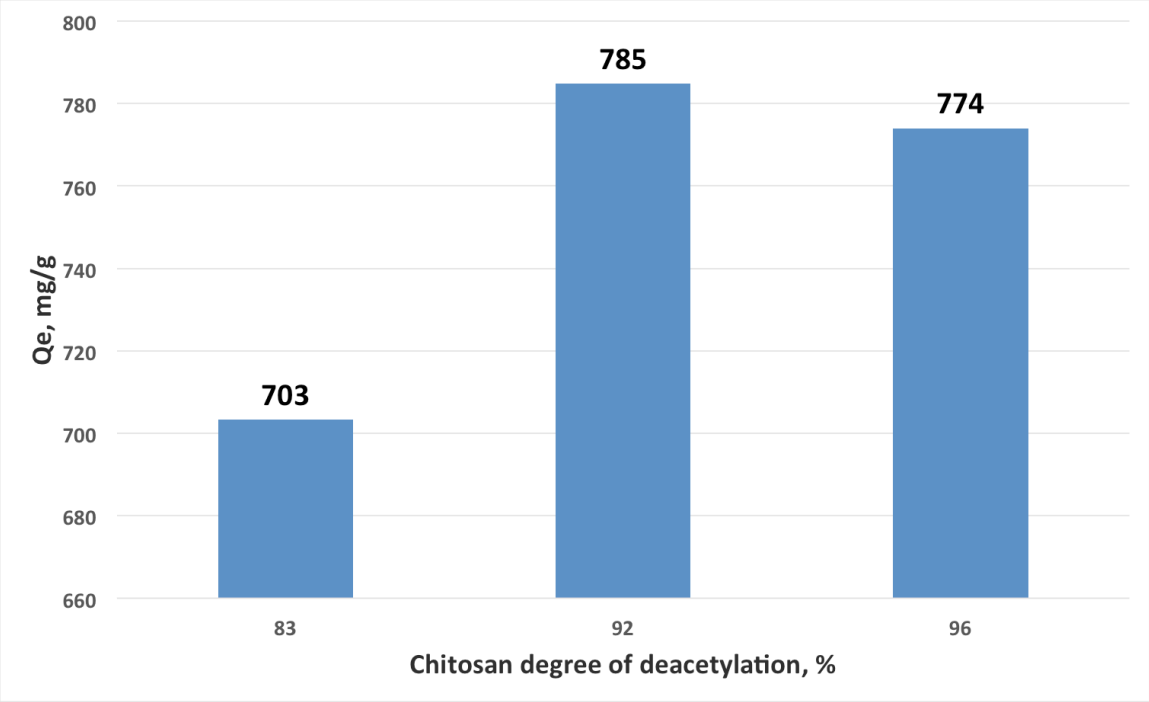
1. CHITOSAN PROPERTIES

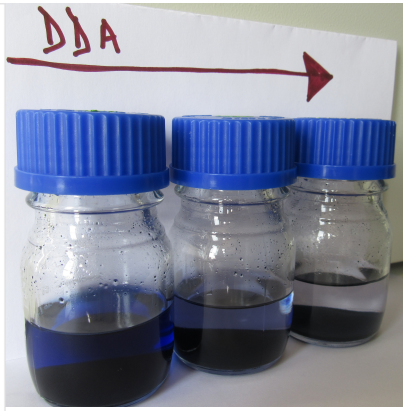
Batch	CS DDA, %	CS viscosity, CPS	Yied, %	Particle size Dv/Dn, µm/µm	Qe[1] Cu^{2+}, mg/g
MagCS3_1	83	53	72	169/46	104.9
MagCS1_2	92.2	42	99	191/73	109.1
MagCS2_1	96.1	35	93	148/43	99.5

[1] Cu^{2+} adsorption conditions: 0.1g adsorbent, C_i = 3.52mg/ml, pH=4.4



Anionic dye adsorption (Reactive Blue 19)





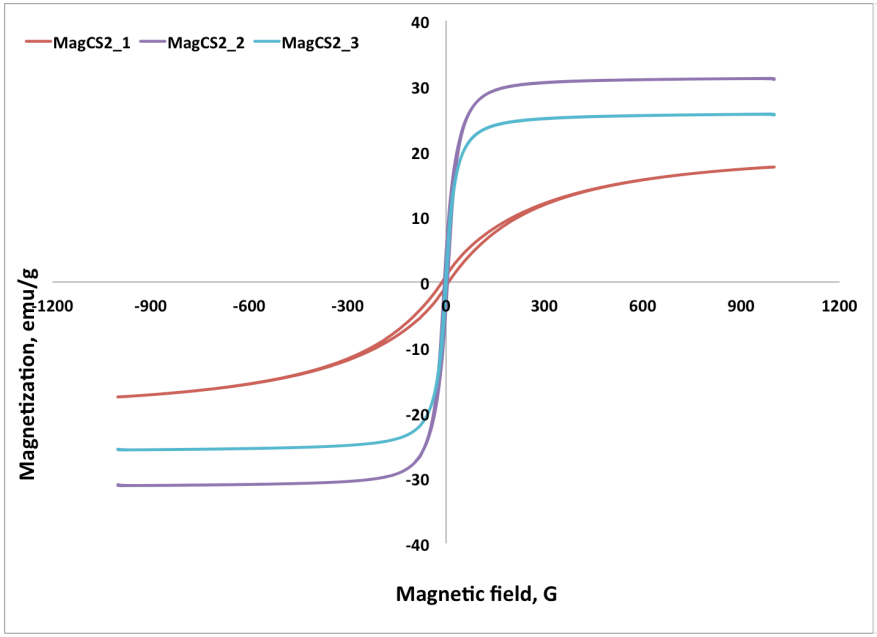
- 0.05g adsorbent,
- dye initial concentration 0.8mg/ml,
- pH=3.4

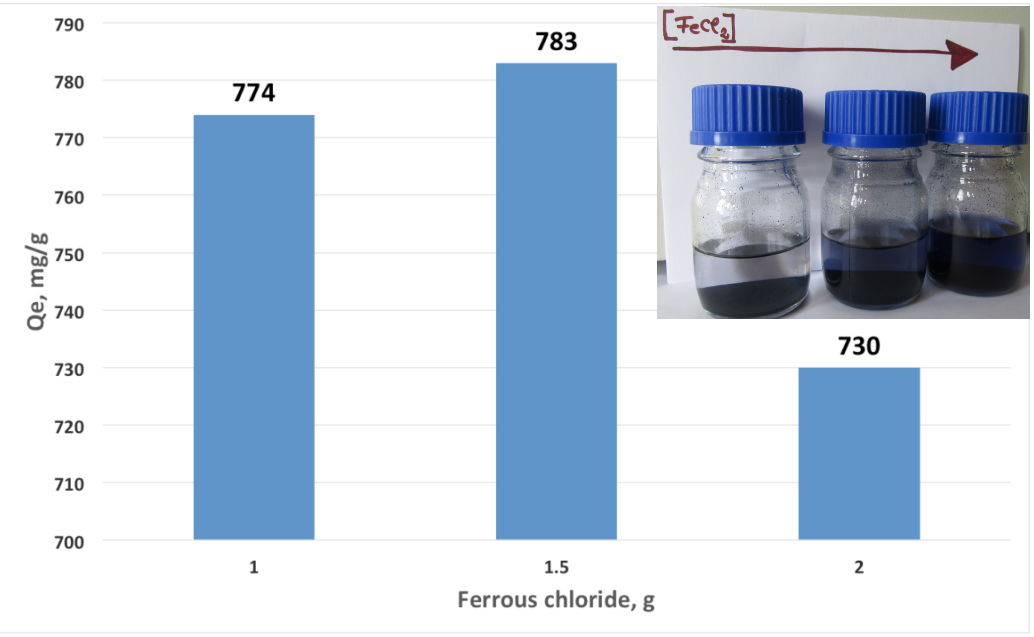
Dye adsorption by electrostatic attraction

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

2. FERROUS CHLORIDE AMOUNT

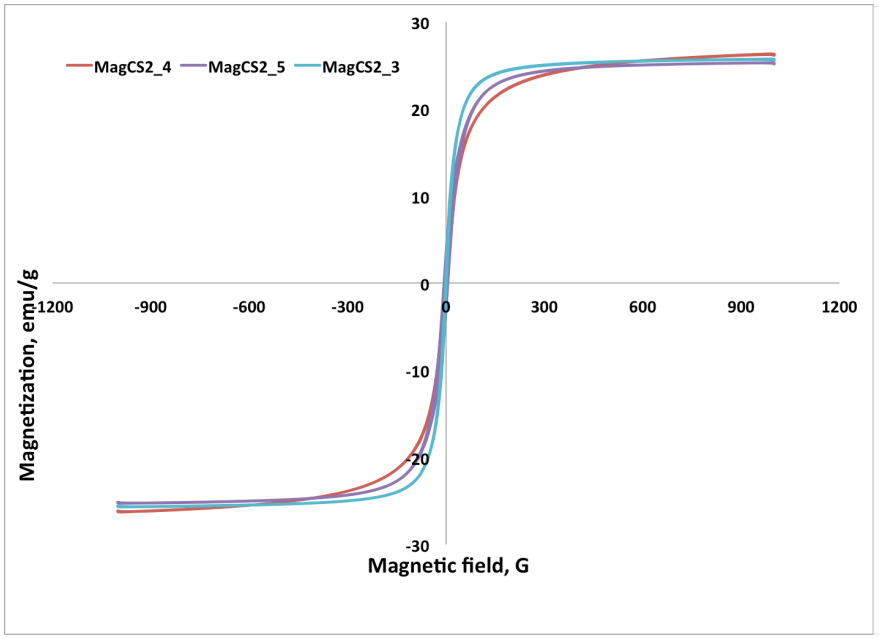
Batch	$FeCl_2.4H_2O$ g	$[NH_3]$ M	[GA] %	Particle size Dv/Dn, µm/µm	Yied, %
MagCS2_1	1	0.5	5	148/43	96
MagCS2_3	1.5	0.5	5	119/55	75
MagCS2_2	2	0.5	5	268/186	82

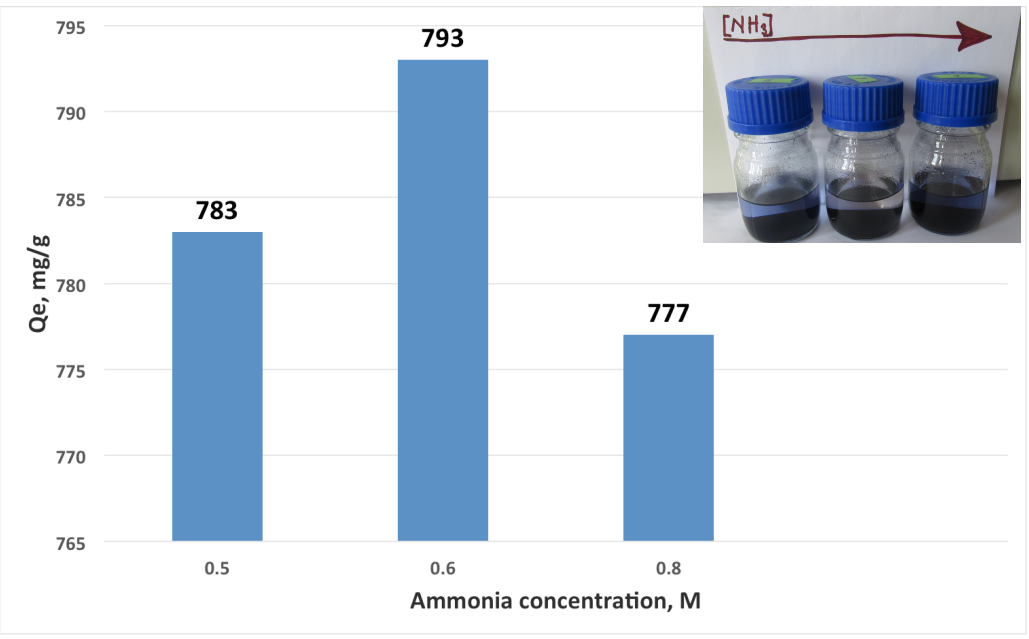




3. AMMONIA CONCENTRATION

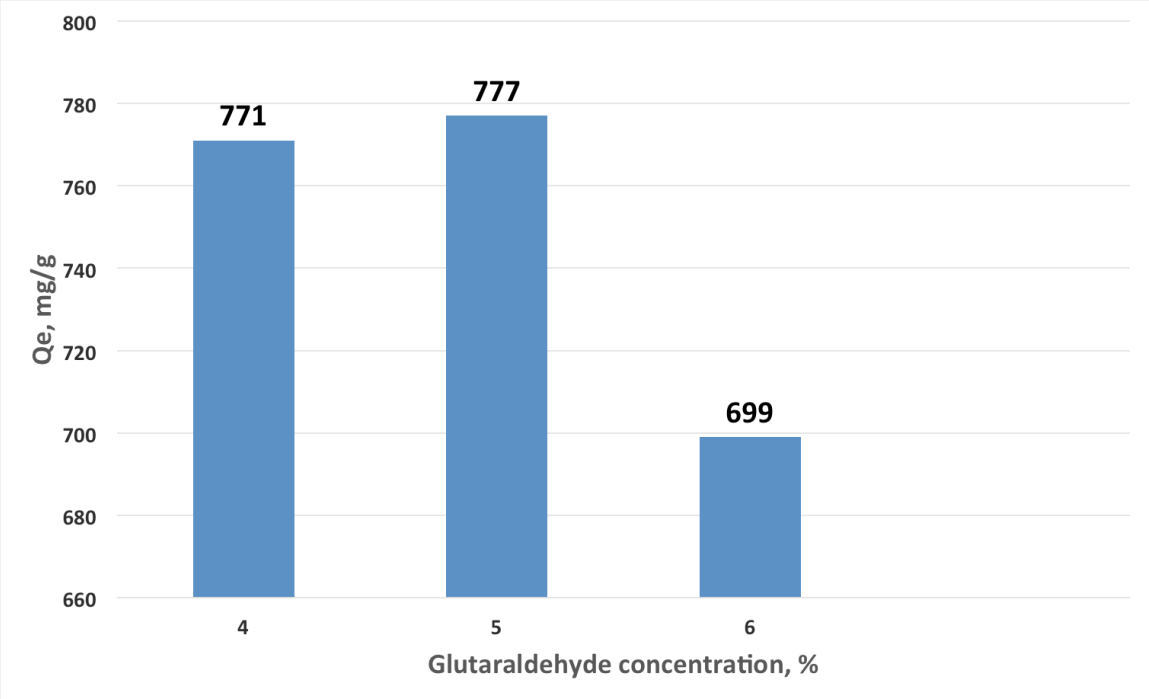
Batch	$FeCl_2.4H_2O$ g	$[NH_3]$ M	[GA] %	Particle size Dv/Dn, µm/µm	Yied, %
MagCS2_3	1.5	0.5	5	119/55	75
MagCS2_4	1.5	0.6	5	193/77	82
MagCS2_5	1.5	0.8	5	239/146	89

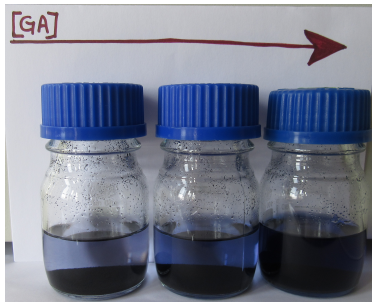




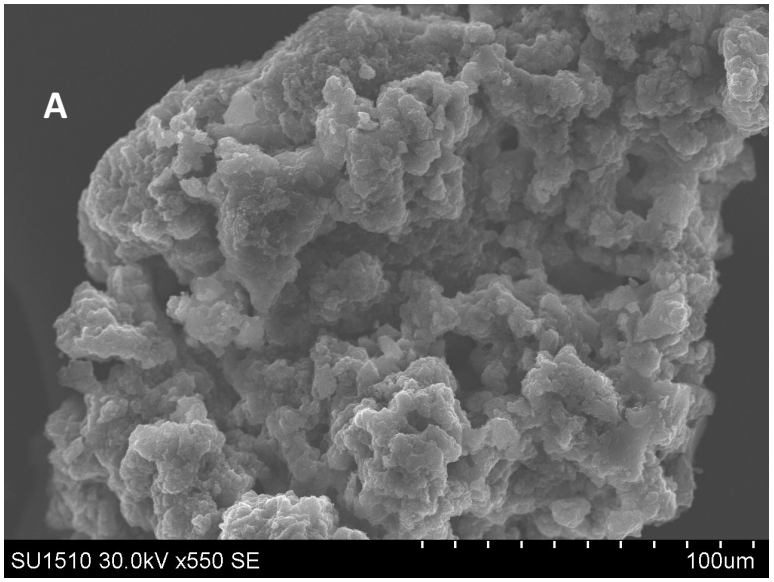
4. GLUTARALDEHYDE CONCENTRATION

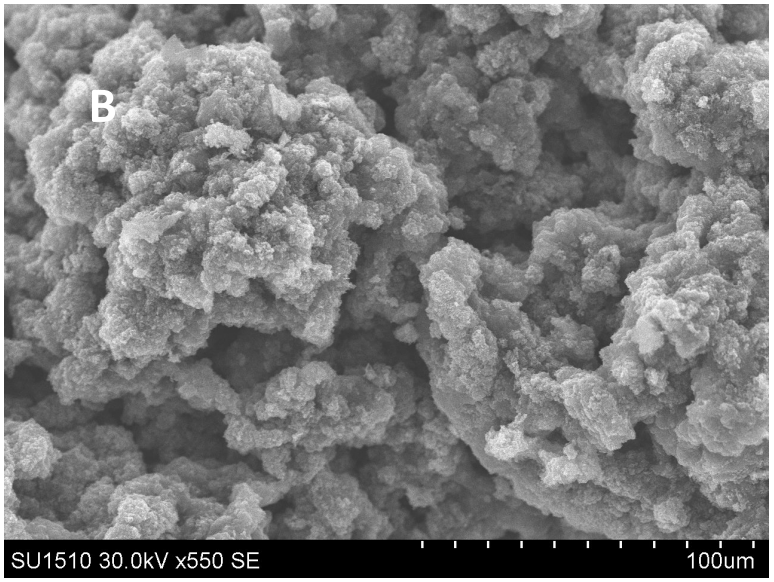
Batch	$FeCl_2.4H_2O$ g	$[NH_3]$ M	[GA] %	Magnetization, emu/g	Particle size Dv/Dn, µm/µm	Yied, %
MagCS2_7	1.5	0.8	4		119/55	92
MagCS2_5	1.5	0.8	5	26.1	193/77	89
MagCS2_6	1.5	0.8	6		239/146	96





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

Conclusions

- The synthesis procedure is robust with respect to chitosan variability within the investigated range
- Magnetization may be increased by using more iron salt
- The ammonia concentration needs re-optimization when the iron salt amount is changed
- Adsorption capacity may be increased by decreasing the crosslink level
- Anionic dye adsorption is a simple and sensitive method to characterize the product with respect to the surface concentration of amino groups
- Future work: scale-up synthesis; optimize cleaning procedure; reproducibility study

Acknowledgements

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

- Celina Alexandrica

THANK YOU FOR YOUR ATTENTION!