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### Evaluation of magnetic chitosan composite as a green adsorbent for removal of Reactive Orange 16 (RO16) from simulated wastewater

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# Introduction/motivation

### Synthetic dyes

- $\checkmark$  toxic to human;
- $\checkmark$  resistant to aerobic degradation;
- ✓ stable in oxidizing agents;
- $\checkmark$  dye wastes are toxic;
- ✓ may be carcinogenic;
- ✓ industrial use (leather, cosmetic, printing).

#### Removal methods

✓ chemical coagulation, activated sludge, biodegradation, oxidation, membrane separation, photodegradation and adsorption.

#### \* Magnetic adsorbents

> magnetic iron oxide particles, magnetic nanocomposite adsorbents with polymeric supports, magnetic composites containing agricultural waste

✓lower cost;

- ✓ stability;
- ✓ biocompatibility;
- $\checkmark$  reactive surface.

## Introduction/motivation

#### Raw material



#### > Magnetite-CS-composite (MagCS):

- ✓ easy separation;
- ✓ environmentally friendly;
- $\checkmark$  good adsorption capacity.

### **Objectives**

**Main objective:** synthesize magnetic chitosan as a novel-green magnetic adsorbent material.

✓ Magnetic composite synthesis;

 $\checkmark~$  Characterization before and after adsorption;

 $\checkmark\,$  Adsorption studies;

- ✓ Desorption and re-use studies;
- ✓ Conclusions and future work.

### **Magnetic composite synthesis**



The chitosan magnetic particles were synthesized in alkaline conditions by mild oxidation of the ferrous ions initially dispersed uniformly within the polysaccharide matrix.

- 1. FeCl<sub>2</sub> is dispersed in acetic acid CS solution;
- 2. CS precipitation by adding ammonia solution;
- 3. partial oxidation of ferrous ions by adding KNO<sub>3</sub>: magnetite (Fe<sub>3</sub>O<sub>4</sub>);
- 4. crosslinking the CS matrix with glutaraldehyde (GA);
- 5. acid-base treatment: colloidal and stabilized suspension.

### Characterization





Figure 1 Magnetization measurements of MagCS



Figure 2 SEM image (a) and size distribution histogram (b) of MagCS



Adsorption parameter optimization: ✓Initial RO16 concentration: from 0.1 to 1.87 mg/mL; ✓Contact time: from 0.5h to 26h at 150 rpm; ✓Temperature: between 9.5°C and 55°C; ✓Initial pH: in the range of 2.23 - 9.73.

#### a. Adsorption experiments



#### **b.** Adsorption isotherms



#### Table 2 Constants obtained from the adsorption isotherms

Constants/Material	MagCs-RO16			
	R <sup>2</sup>	0.9998		
Langmuir	$q_m(mg/g)$	1428.57		
	$K_{L}(mL/mg)$	140		
	R <sub>L</sub>	0.0007		
	R <sup>2</sup>	0.9778		
Freundlich	$K_{\rm F}({\rm mg/g})({\rm mg/mL})^{1/{\rm n}}$	402.43		
	n	12.85		
	R <sup>2</sup>	0.8638		
<b>Dubinin-Raduskevich</b>	$X_m(mg/g)$	1106.10		
	$K_{DR}(mol^2/kJ^2)$	1.1685		
	E <sub>s</sub> (kj/mol)	0.654		

#### c. Adsorption kinetics



Table 3 The results of the adsor	ption kinetics studies for the adsor	ption of RO16 on MagCS composi	ite
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Pseudo first order model			Pseudo second order model			Intra-particle diffusion model		
q <sub>e exp</sub> (mg/g)	q <sub>e calc</sub> (mg/g)	k <sub>1</sub> (h <sup>-1</sup> )	R <sup>2</sup>	q <sub>e calc</sub> (mg/g)	k <sub>2</sub> (g/mg·h <sup>-1</sup> )	R <sub>2</sub>	k <sub>id</sub> (mg/g·h <sup>o.5</sup> )	R <sup>2</sup>
1409.79	114.28	0.564	0.95	1487.57	0.012	1	18.006	0.50

#### d. Effect of temperature and the themodynamic data



Table 4 Thermodynamic results for the adsorption of RO16 on MagCS composite

Thermodynamic parameters							
Material		Δ	ΔH (k.I/mol)	ΔS (I/mol.K)			
	9.5°C	25°C	35°C	45°C	55°C		(3/1101*1X)
MagCs-RO16	-25.01	-25.49	-25.80	-26.11	-26.42	-16.24	31.02

#### e. Desorption and re-use studies

**Table 5** Desorption and re-use results

Sample	Desorpti	Re-use 1 (q <sub>e</sub> , mg/g)		
	NaOH (pH=11)	NaOH + non-ionic surfactant (pH=11)	Initial	Re-used
MagCs-RO16	76.41	80.04	1409	1288.29 1242.08
	Desorpti	Re-use 2 (q <sub>e</sub> , mg/g)		
	NaOH	NaOH + non-ionic surfactant	Initial	Re-used
	(pH=11)	(pH=11)	1288.29	1263.24
	91.69	94.40	1242.08	1238.33

### **EDX analysis**

➢ before adsorption



#### ➤ after adsorption



#### Wastewater experiment



1. Simulated wastewater:  $- 1g/L \text{ NaCl}, 1g/L \text{ Na}_2\text{CO}_3, 1mg/mL \text{ RO16}$ 

- cotton, 1h, 50°C

2. Adsorption 24 h: Qm=713.25 mg/g.

n= 97.73 %

# Conclusions

- MagCS was synthesized, characterized and successfully used for RO16 adsorption.
- The effects of various parameters (pH, contact time, temperature and initial dye concentration) on the adsorption were studied.
- The adsorption process was fitted into three isotherm models: Langmuir, Freundlich and Dubidin-Radushkevich and three kinetic models: pseudo first order, pseudo-second order and Webber-Morris;
- The maximum adsorption capacity obtained for RO16 was 1409.79 mg/g;

**Future work**: Simulated wastewater studies: influence of the anionic species contained in the wastewater on the adsorption capacity of the magnetic adsorbent.

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THANK YOU FOR YOUR ATTENTION !!!