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## ELIMINATION OF METHYLENE BLUE FROM SYNTHETIC AQUEOUS SOLUTIONS BY ABSORPTION ON CHITOSAN COMPOUNDS WITH SYNTHETIC HYDROXIAPATITIS

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### **Introduction**

Dyes, one of the common pollutants in wastewater, are chemical compounds that have complex organic molecular structures. Most dyes are poor biodegradable and toxic, which not only affects the environment but also threatens biological health. Water pollution associated with the discharge of dyes from the textile industry is one of the significant threats to ecosystems. Dyes are considered hazardous pollutants by various major environmental agencies, including the United States Environmental Protection Agency (US EPA). The presence of dyes in water, even in low concentrations, can have negative effects on the environment due to their carcinogenic nature. The development of cheap, simple, effective and ecological techniques for the removal of dyes in wastewater is mandatory, in order to prevent their harmful effects. Consequently, extensive research has been initiated to develop new effective techniques for the remediation of wastewater containing dyes.

### **Materials and methods**

The synthesis and characterization of chitosan composites with synthetic hydroxyapatite was performed by collaborators from the Polytechnic University of Bucharest through the project Project no. 92/01.07.2014, Innovative materials and processes for the selective removal of heavy metals from wastewater, Acronym HAP-CHIT-MAG, Project code: PN-II-PT-PCCA-2013-4-0418.

The experiments were carried out under optimal conditions with MB solutions of the following concentrations: 100 mg/L; 75 mg/L; 50 mg/L; 25 mg/L; 5 mg/L. The contact time between the MB solution and the CHIT-HAP composite was 4 hours (enough to reach equilibrium), the amount of CHIT-HAP was 20 mg, the volume of the MB solution was 20 mL and the pH range 2.55-10.

### **Results and conclusions**

In the experiments performed, HAP samples were used for the preparation of synthesized CHIT-HAP composites at different calcination temperatures. For example, the sample of HAP synthesized in the presence of microwaves determined the CHIT-HAP-1 composite consisting of well-shaped hexagonal HAP crystallites,

unevenly distributed in the amorphous chitosan polymeric matrix. From the HAP sample calcined at 850°C, the CHIT-HAP-2 composite was prepared consisting of nanometric aggregates of HAP with elongated shape dispersed in the polymer matrix. The sample of HAP calcined at 600°C led to the CHIT-HAP-3 composite consisting of cylindrical HAP-shaped nanoparticles dispersed in the polymeric chitosan matrix. It was also observed that the decrease in the calcination temperature of HAPs had as a consequence the increase of the porosity of the CHIT-HAP composites (Figure 1).

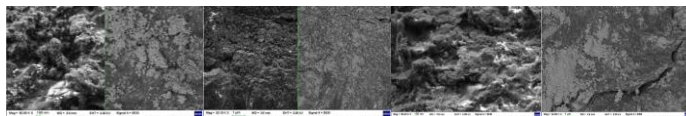


Fig 1. SEM images for CHIT-HAP composite

In order to determine the effect of the morphological and structural characteristics of CHIT-HAP composites, batch experiments were performed on the remediation of aqueous solutions with methylene blue (MB). The optimal conditions of the studied remediation process were determined from experiments in which the pH and contact time varied in the solutions used in the remediation process. The results revealed that the CHIT-HAP-1 composite has a maximum MB retention capacity (determined from the nonlinear Langmuir isotherm) of 37.56 mg/g, the CHIT-HAP-2 composite a retention capacity of 38.89 mg/g, and the CHIT-HAP-3 composite is characterized by a retention capacity value of 44.70 mg/g (Figure 2 and Figure 3).

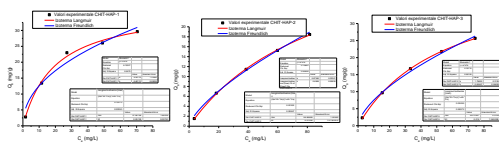


Fig 2. Nonlinear isotherms characteristic

| Adsorbent            | CHIT-HAP-1 | CHIT-HAP-2 | CHIT-HAP-3 |
|----------------------|------------|------------|------------|
| Parameter Langmuir   |            |            |            |
| $Q_m$ (mg/g)         | 37.5620    | 38.8899    | 44.7035    |
| $K_L$ (L/mg)         | 0.0331     | 0.0109     | 0.018      |
| $R^2$                | 0.9935     | 0.9995     | 0.9997     |
| $R_{L1}$             | 0.1631     | 0.4783     | 0.3571     |
| AIC                  | 26.0942    | 8.7803     | 8.9109     |
| Parameter Freundlich |            |            |            |
| $K_F$ (mg/g)         | 4.3538     | 0.8733     | 1.7845     |
| $1/n$                | 0.4611     | 0.6989     | 0.6245     |
| $R^2$                | 0.9475     | 0.9994     | 0.9913     |
| AIC                  | 36.5632    | 18.3983    | 26.1202    |

Fig 3. Parameters of Langmuir and Freundlich equations

The isothermal study revealed that the process of remedying aqueous dye solutions can be described as a monolayer adsorption process on the homogeneous surface of CHIT-HAP composites. The kinetic study showed that the mechanism involved in the process of remedying aqueous solutions with methylene blue is represented by chemical interactions between methylene blue groups and functional groups grafted on the surface of the tested composites. In conclusion, applying a simple method and without high costs, morphologically different CHIT-HAP composites are prepared, material which are highly effective in dyes elimination from wastewater samples.

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