# Curcumin@MgO/graphene oxide nanoadsorbents for the removal of fluoride from wastewaters

***Konstantinos N. Maroulas, Athanasia K. Tolkou, Anastasia D. Meretoudi, Sofia L. Kouvalakidou, Ramonna I. Kosheleva, Ioannis Georgiou, Despina A. Gkika, Athanasios Varoutoglou, Irene Moschou, Pavlos Efthymiopoulos, George Z. Kyzas***

***Hephaestus Laboratory, Department of Chemistry, School of Science, Democritus University of Thrace, Kavala, Greece***

***(E-mail: tolkatha@chem.ihu.gr)***

## Introduction

Fluoride in drinking can cause a variety of ailments, the most frequent of which is fluorosis. The permissible level of fluoride in drinking water set by WHO is considered to be 1.5 $mgL^{-1}$. As a result, there is an urgent need to remove fluoride from drinking water. The current study recommends the usage of adsorbents based on graphene oxide (GO). GO has recently been proved to be a viable adsorbent for wastewater treatment due to its superior mechanical, physical, and chemical characteristics. Chitosan (Cs) is a natural polysaccharide holding both active amino and hydroxyl groups, which can be modified to obtain desired properties. Curcumin (Cur) has been used as reducing and conjugating agent for metal oxide nanoparticles. Previous studies have shown that Mg plays an important role for the removal of fluoride inions, and for this reason was chosen as the modification agent.

## Results & Discussion

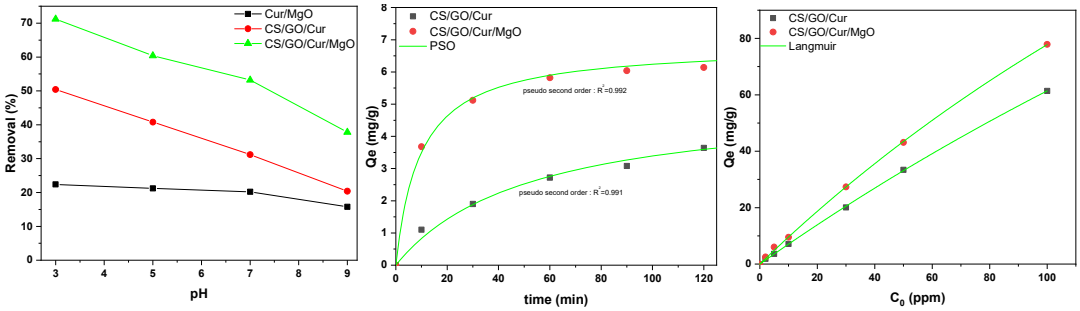



Figure 1: Effect of pH (**left**), of contact time (**middle**) and adsorption isotherms (**right**) on fluoride adsorption; initial $F^-$ concentration 5 mg/L for pH and contact time (pH 3) and 2-100 mg/L for isotherms (pH 3), dose 0.5 g/L,T=298 K

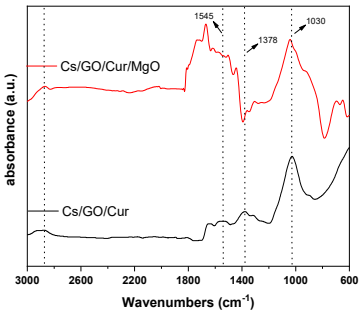



Figure 2: FTIR diagrams

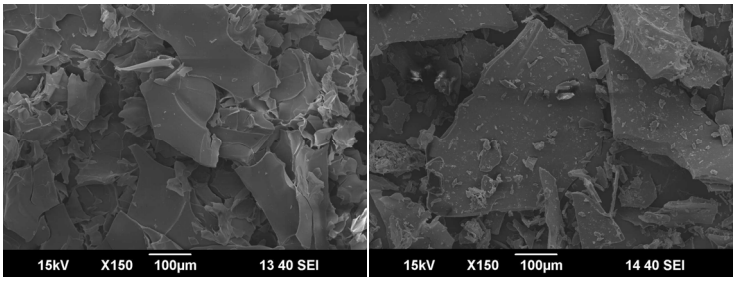
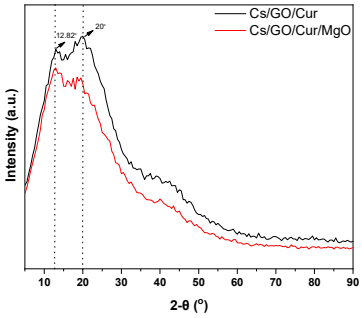



Figure 3: SEM images Cs/GO/Cur (**left**) and Cs/GO/Cur@MgO (**right**)

In batch experiments, the effect of the initial solution pH was studied to determine the feasibility of CS-GO-Cur@MgO for $F^-$ removal. As illustrated in Figure 1, the maximum $F^-$ removal was observed at pH 3.0. The modification of the material showed advanced adsorption capacity, when comparing the results with those obtained by the less complex materials (Cur/MgO and Cs/GO/Cur). The experimental data fitted better to the PSO kinetic model, indicating that the adsorption of $F^-$ was closer to chemical adsorption. In addition, the Langmuir isotherm model was found to better fit the adsorption, which describes the monolayer adsorption on the homogeneous surface of the adsorbent.

The morphology and structure of the materials, were observed by SEM (Fig. 3) and FTIR (Fig. 2). As shown in Figure 3, Cs/GO/Cur has sheet-like shape particles, showcasing a smooth surface. MgO particles add a rough texture to the material. From the SEM analysis it is observed that MgO has a good distribution within the matrix.




| | SA ($m^2$/g) | avg Pore Size (Å) | Pore Volume ($cm^3$/g)@STP |
|---|---|---|---|
| Cs/GO/Cur | 140 | 20 | 122 |
| Cs/GO/Cur@MgO | 370 | 24 | 220 |

Figure 4: XRD of adsorbents (**left**), structural properties (**middle**) and Thermodynamic parameters (**right**)

The BET surface area ($m^2$/g), total pore volume ($cm^3$/g), and average pore size (Å) of the materials (Fig. 4) were measured. As shown, the surface area of Cs/GO/Cur@MgO was extremely raised by adding MgO (from 140 to 1780 $m^2$/g). According to XRD patterns, the samples have a broad peak centered at 2θ = 14° which corresponds to the 002 carbon reflection.

| | T (K) | $\Delta G^0$ (kJ/mol) | $\Delta H^0$ (kJ/mol) | $\Delta S^0$ (kJ/mol·K) | $R^2$ |
|---|---|---|---|---|---|
| CS/GO/Cur | 303 | -17.137 | 0.017 | 0.0566 | 0.9917 |
| | 313 | -17.703 | | | |
| | 323 | -18.269 | | | |
| CS/GO/Cur/MgO | 303 | -1.510 | 16.093 | 0.0581 | 0.9377 |
| | 313 | -2.091 | | | |
| | 323 | -2.672 | | | |

Figure 5: Thermodynamic parameters

According to thermodynamics (Fig. 5), a positive value of $\Delta H^0$ suggests the endothermic nature of the process. $\Delta G^0$ values are negative recommending that the process is spontaneous. The positive value of $\Delta S^0$, indicates that there is an increase in random interaction between solid/liquid interfaces.

## Conclusions

- The incorporation of MgO increased the adsorption efficiency for the removal of fluoride ions significantly, while capacity was increased from 371 to 420 mg/g
- It was found that at pH 3.0 ± 0.1, with the addition of 0.5 g/L the removal rate reached over 70 %.
- The Langmuir isotherm model and the pseudo-second order kinetic model were found to better fit the adsorption, concluding that the adsorption of $F^-$ on adsorbents was monolayer and closer to chemisorption.
- According to thermodynamics, there is a positive value of $\Delta H^0$ that suggests the endothermic nature of the process.
- Finally, the addition of MgO had a huge impact on structural properties, highly boosting both specific area and pore volume.

**Acknowledgment**

**We acknowledge support of this work by the project "Advanced Nanostructured Materials for Sustainable Growth: Green Energy Production/Storage, Energy Saving and Environmental Remediation" (TAEDR-0535821) which is implemented under the action "Flagship actions In interdisciplinary scientific fields with a special focus on the productive fabric" (ID 16618), Greece 2.0 – National Recovery and Resilience Fund and funded by European Union NextGenerationEU.**

GreenMat
Greece 2.0 NATIONAL RECOVERY AND RESILIENCE PLAN
Funded by the European Union NextGenerationEU