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Chitosan/Graphene oxide@Lignin nanoparticles for the removal of hexavalent chromium from wastewaters

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Introduction

- Water contamination poses a serious threat to environmental health. Among pollutants, chromium (Cr) ions in wastewater are particularly concerning, especially Cr(VI). Due to its hazardous nature, Cr(VI) discharge into water bodies is strictly limited to a maximum of 0.05 mg/L (WHO).
- Adsorption emerges as a highly effective wastewater treatment method due to its affordability, simplicity, and eco- friendliness. A wide range of adsorbent materials are available, and carbon-based adsorbents are among the most effective. Therefore, a new composite material, Cs/GO/LNP consisted of graphene oxide (GO), chitosan (Cs) and lignin nanoparticles (LNP), is employed for the removal of Cr(VI), taking into account the advantages of each additive.
- Hence, Cs is a biopolymer with outstanding adsorption capabilities, that could be due to the numerous functional groups appeared on its structure, such as hydroxyls (−OH) and amines ($-NH_2$). On the other hand, LNP, a natural polymer derived from the paper industry, complements chitosan by providing mechanical reinforcement and diverse functional groups that enhance chemical affinity and electrostatic interactions. Graphene oxide adds high surface area and exceptional mechanical strength, further enhancing the composite's performance and structural integrity.

Results & Discussion

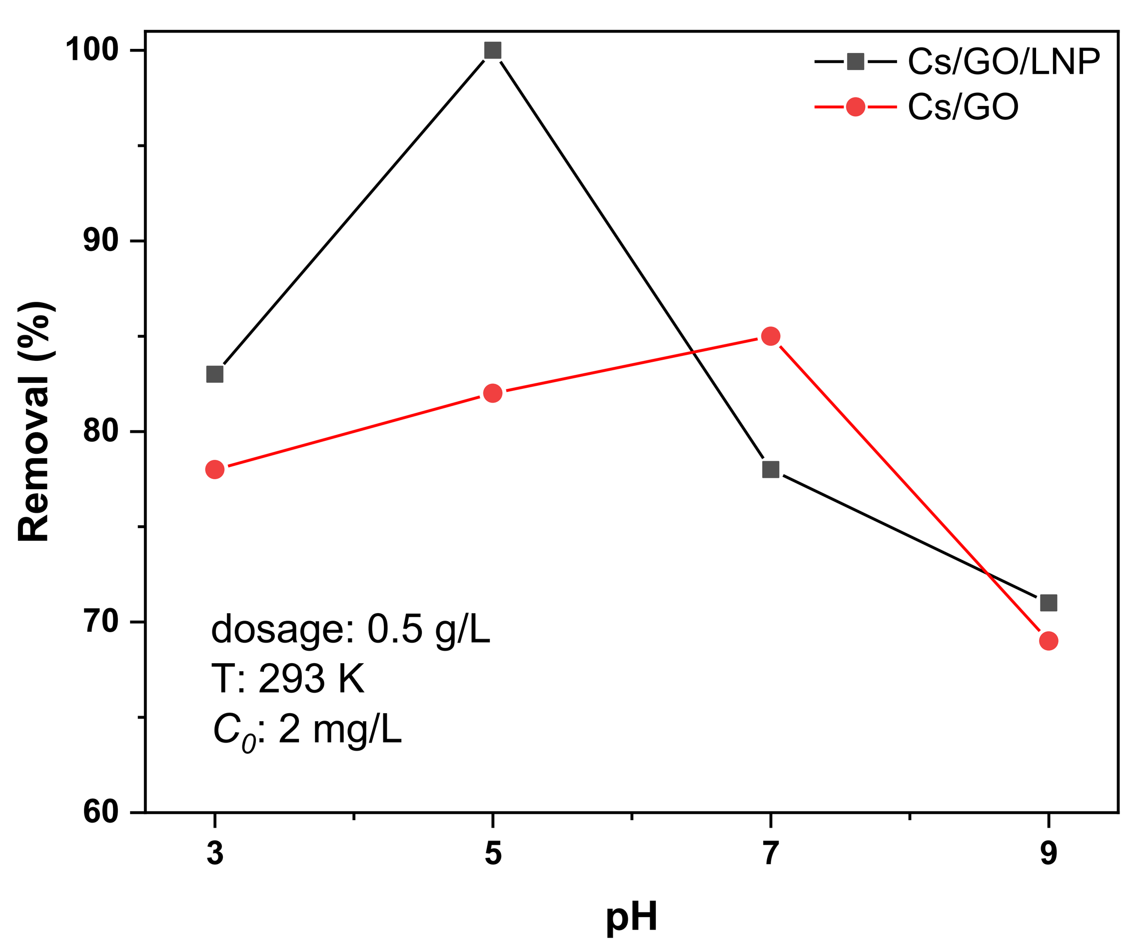


Fig. 1. Effect of pH

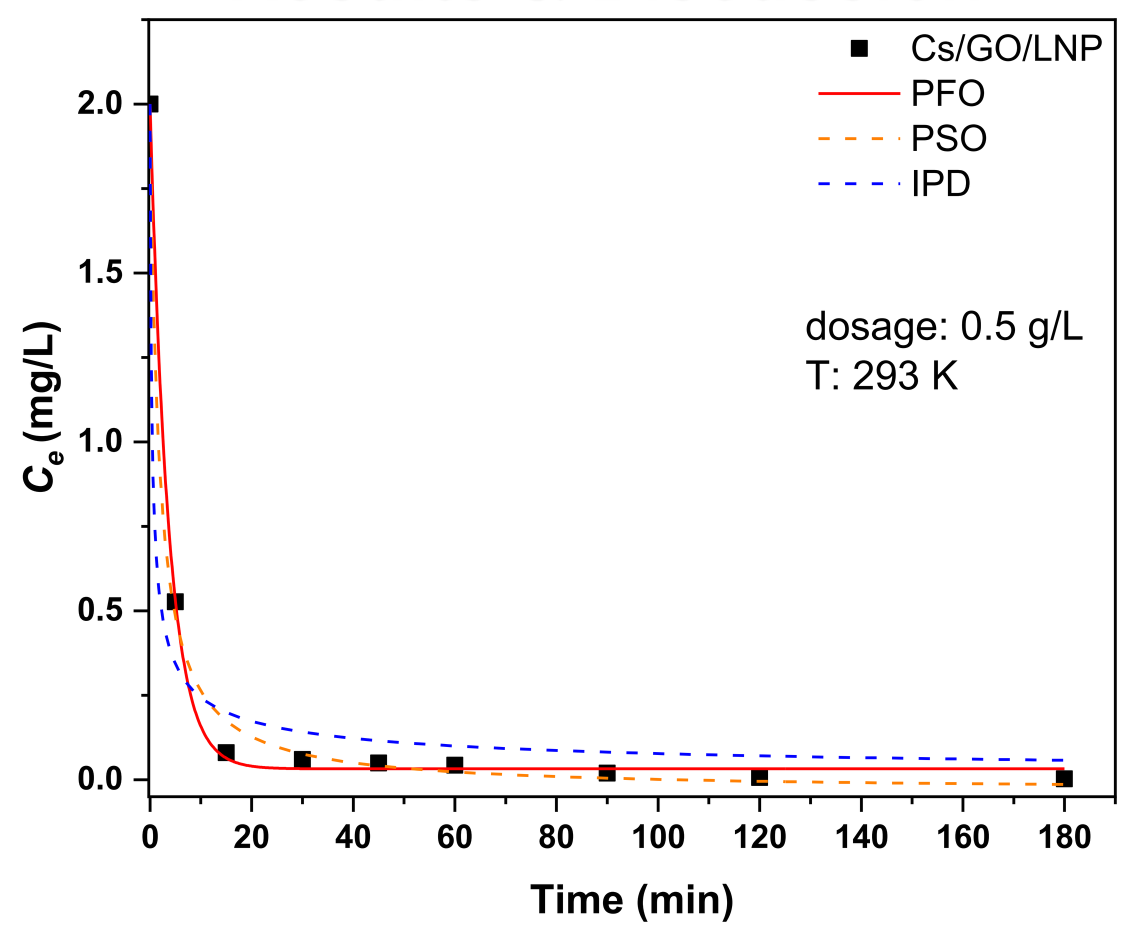


Fig. 2. Effect of contact time

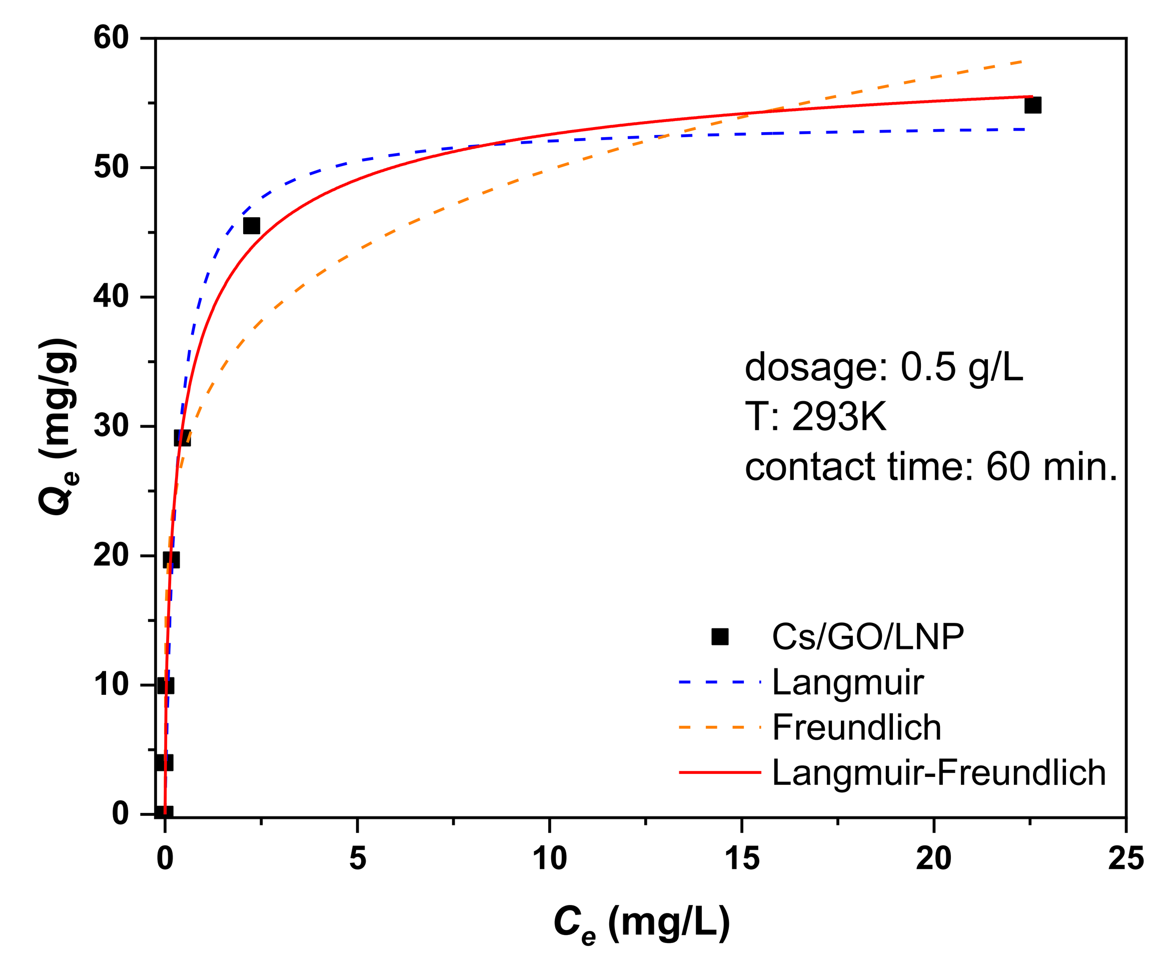


Fig. 3. Isotherm studies

Table 1. PFO, PSO and IPD parameters for the adsorption of Cr(VI)

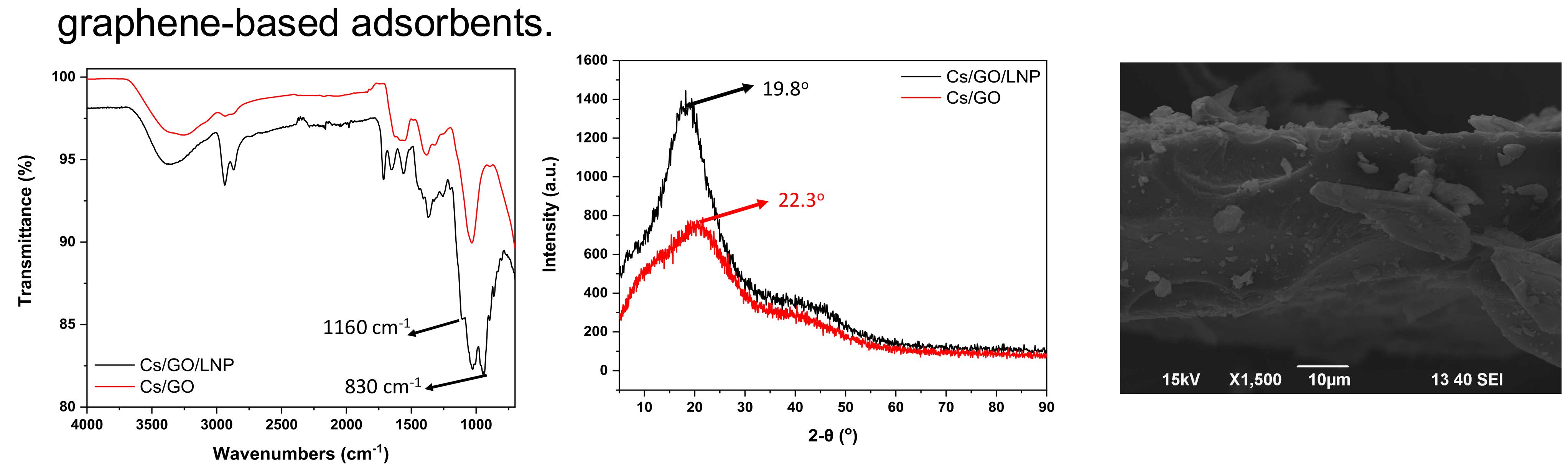
Pseudo-first order model		Pseudo-second order model		Intra-particle diffusion model	
K_1 (1/min)	R^2	K_2 (L/mg·min)	R^2	K_{IPD} (mg/g·min$^{0.5}$)	R^2
0.275	**0.998**	0.587	0.995	3.310	0.975

- ✓ 3 isotherm models, Freundlich, Langmuir and Langmuir-Freundlich, were used for the Cr(VI) adsorption (Fig. 3 and Table 2).
- ✓ The Langmuir-Freundlich isotherm model was found to fit better the experimental adsorption data, indicating surface heterogeneity.

Table 2. Constants of Freundlich, Langmuir and Langmuir-Freundlich isotherm models.

Freundlich isotherm model			Langmuir isotherm model			**Langmuir-Freundlich isotherm model**		
1/n	K_F (mg/g)·(L/mg)$^{1/n}$	R^2	Q_m (mg/g)	K_L (L/mg)	R^2	Q_m (mg/g)	K_{LF} ((L/mg)$^{1/b}$)	R^2
0.187	31.96	0.939	53.71	3.15	0.967	**60.83**	**1.57**	**0.986**

- ✓ According to Fig. 1 the removal of Cr(VI) is favored at acidic environments. Specifically, the highest removal was achieved at pH= 5.0 ± 0.1 (100%) by applying 0.5 g/L of Cs/GO/LNP in 2 mg/L of Cr(VI). Moreover, as depicted, the incorporation of LNP in the structure of Cs/GO increased the adsorption efficiency.
- ✓ As illustrated in Fig. 2, and tabulated in Table 1, the adsorption kinetics followed better the PFO model, indicated that the adsorption was closer to physisorption. According to the kinetics, the equilibrium was reached at 60 min.
- ✓ FTIR studies (Fig 4(a)) confirmed the presence of LNP, due to the introduction of 2 new peaks at 830 and 1160 cm^{-1}, that correspond to syringyl and guaiacyl units of lignin. SEM (Fig 4(c)) revealed a smooth surface, which is characteristic for graphene-based adsorbents.



(a) (b) (c)

Fig. 4. (a) FTIR, (b) XRD, (c) SEM.

Conclusions

- Chitosan/Graphene oxide/Lignin Nanoparticles (Cs/GO/LNP), have been synthesized, for enhanced adsorption capacity towards Cr(VI).
- At pH 5.0 ± 0.1, with the addition of 0.5 g/L the removal rate reached 100%.
- The adsorption data fitted better to Langmuir-Freundlich isotherm model, whereas the adsorption kinetics followed better the pseudo-first-order model. Thus, the adsorption of Cr(VI) on was closer to physisorption.
- The adsorption procedure met equilibrium at 60 minutes, while maximum adsorption capacity Q_m reached 60.83 mg/g, according to Langmuir-Freundlich.
- Findings from FTIR, XRD and SEM confirmed the successful synthesis of Cs/GO/LNP.

Acknowledgment

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