Reduced graphene oxide/chitosan/starch/curcumin doped with ZnO for the removal of fluoride ions from wastewaters

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Abstract
Fluoride is an important inorganic substance that's present in the natural world in different concentrations and forms, both naturally and as a result of human activity. However, elevated fluoride concentrations can cause serious difficulties in both human and animal bodies [1]. The World Health Organisation (WHO) defines an acceptable level of 0.5-1.5 mg/L in drinking water. The common methods for fluoride removal from drinking water are chemical precipitation, membrane processes, ion-exchange, and adsorption. Adsorption shines among the other methods, as it is generally a fast reaction and relatively inexpensive compared to other processes [2].
The current study recommends the usage of adsorbents based on reduced graphene oxide (rGO). Graphene oxide (GO) has been proved to be a viable adsorbent for wastewater treatment due to its superior mechanical, physical and chemical characteristics [3]. Nevertheless, since graphene sheets are composed of hexagonally organised sp^2 carbon atoms, they can solely adsorb adsorbates via van der Waals forces. Therefore, without alterations graphene is not an effective absorbent for many pollutants [4]. rGO is a novel carbon-based material with extraordinary traits such as a large surface area, superior electrical and mechanical features [5]. It exhibits electrostatic interaction, structural conjugation, many defects, residual oxygen functionality, π-π interaction, and high porosity levels. Starch is a renewable and biodegradable material, that has high hydroxyl units content. Hence, adding starch can lower the cost of pure graphene and can hinder graphene agglomeration [6]. Chitosan is a natural polycationic linear polysaccharide holding both active amino groups and hydroxyl groups, which can be modified to obtain certain desired properties [7]. rGO was also grafted with ZnO nanoparticles (nps). Metal oxide-based nanomaterials were shown to be extremely successful adsorbents, removing heavy metal and metalloid ions at very low concentrations [8]. Curcumin (Cur) is a natural polyphenolic substance derived from the plant Curcuma longa L. Previous research has shown that encapsulating curcumin in nanoparticles improves its capacity to absorb metal ions as a chelating agent [9].
The composites' morphology and structure were characterized by FT-IR, SEM, BET and XRD analysis. The effect of the pH value, contact time, adsorbent's dosage and initial fluoride concentration was examined in order to evaluate the adsorption efficiency of the materials. According to the results, the modification of Cs/Starch/GO@Cur with ZnO nps increased the removal of fluoride ions, by using 1.0 g/L of the adsorbent. Experimental data of equilibrium were used to calculate adsorption isotherms at temperatures of 30°C, 45°C and 60°C and the obtained data were fitted to the Langmuir and Freundlich adsorption isotherm models. The optimum solution pH value of the adsorption process was found and the kinetic data were fitted to pseudo-first-order and pseudo-second-order. According to thermodynamics the spontaneous nature of their adsorption was confirmed.

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