Abstract

Contamination of water by fluoride ions is one of the major threats to human life and thus must be removed from drinking water. A novel CeO_2 polypyrrole nanocomposite ($HCeO_2$@PPy) was fabricated by co-precipitation of CeO_2 nanoparticles followed by in situ chemical oxidative polymerization. The as-synthesised adsorbent was characterized using a variety of physico-chemical techniques which included Fourier Transform Infrared Spectroscopy (FTIR), X-Ray diffraction (XRD), Braunauer-Emmett-Teller (BET), Field Emission Scanning Electron Microscopy/Energy Dispersive (FE-SEM/EDS), High Resolution-Transmission Electron Microscopy (HR-TEM), X-ray Photoelectron Spectroscopy (XPS) and point-of-zero charge (pzc) determination. The $HCeO_2$@PPy nanocomposite adsorbent was applied for the removal of F^- ions from aqueous solution. Application of the adsorption modelling, revealed that the Langmuir adsorption isotherm model best described the process with a maximum adsorption capacity of 70.92 mg g^{-1}, at an optimum pH of 6.0 ± 0.2, 0.03 g adsorbent dose and 25 °C. Rapid kinetic studies revealed that the pseudo-second-order model gives a better description of the adsorption process. Thermodynamic data showed that the adsorption process was physical, spontaneous and feasible. The behaviour of the amino functional groups within $HCeO_2$@PPy moiety and the nanometal oxide surface hydroxides at different pHs along with the pH□zc, FTIR and XPS spectra analyses were used to explain the mechanism of adsorption. The mechanism was conceived to be anionic exchange of hydroxyl group with the F^- ions and electrostatic attractions of protonated hydroxyl on the surface of the adsorbent as well as the nitrogen atoms of amino groups from the polypyrrole (PPy) moiety with F^- ions. The determined thermodynamic parameters, enthalpy change ($\Delta H° = -26.33$ kJmol^{-1}) and Gibbs free energy change ($\Delta G°$ = −19.074 to −10.028 kJ mol^{-1}) indicated the exothermic and spontaneous nature of the sorption process. Further evaluation on the as-prepared adsorbent exposed a moderately selective material which exhibited excellent removal ability of F^- ions from ground water at its natural pH to below WHO stipulated levels with an adsorption-desorption efficiency of up to three cycles. Therefore, hydrous CeO_2 polypyrrole nanocomposite has revealed great potential for water defluoridation.