In this study, graphene oxide (GO), polyethyleneimine (PEI) and potassium hydroxide (KOH) were used to synthesize reduced graphene oxide (rGO/PEI-KOH) nanocomposite. The presence and grafting of PEI molecules on the reduced GO surface were assessed by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) analyses. The rGO/PEI-KOH nanocomposite was successfully applied for hexavalent chromium, Cr(VI), wastewater elimination. The resulting rGO/PEI-KOH adsorbent was found to be highly effective for Cr(VI) removal at low pH values and achieved a maximum capacity of experimental adsorption of 398.9 mg/g, which is one of the highest sorption capacity of most GO- and PEI-based adsorbents reported in the literature up to date. Studying the adsorption mechanism, the sorption isotherm revealed that the modified-Langmuir model was the best fit and Cr(VI) removal follows a pseudo-second-order kinetics, with the predominance of intraparticle diffusion during the first step of adsorption. XPS analysis indicated the presence of appreciable amount of Cr(III) on the adsorbent surface, which suggests that the adsorbed Cr(VI) ions were effectively reduced to Cr(III) on the rGO/PEI-KOH adsorbent surface (~70% of the total adsorbed Cr). Cr(VI) adsorption and subsequent reduction to Cr(III) both contributed to the Cr(VI) removal. The results of the present study highlight the benefits of rGO/PEI-KOH like low cost, environmentally friendly, large toxic Cr(VI) ions adsorption capacity and its effective reduction to less-toxic Cr(III)