

The present thesis deals with the synthesis and characterization of nanocomposite of graphene oxide with zirconium oxide (rGO/ZrO<sub>2</sub>) and magnesium oxide (GO/MgO) for the efficient removal of fluoride and lead ions from water. The nanocomposites i.e. rGO/ZrO<sub>2</sub> and GO/MgO showed specific binding capability toward fluoride and lead respectively thus showed excellent adsorption capacity for these ions. For the remediation purpose batch as well as column both methods were applied. The batch adsorption experiments were conducted for both the ion i.e. fluoride and lead for the optimization of various process parameters (pH, initial metal ion concentration, temperature, and adsorbent doses) to achieved the maximum adsorption capacity. In addition to it, column studies were also conducted which is based on the parametric optimization of batch system for the fabrication of treatment plants for the removal of fluoride and lead from the water.

The first chapter has been focussed on the introduction concerning environmental pollution especially water pollution. This work is devoted to the adsorptive remediation of fluoride and lead from water. The excess concentration of fluoride causes dental and skeletal fluorosis, brittle bones, osteoporosis, and arthritis whereas, lead concentration above the permissible limits induces various reproductive, genotoxic, and neurological defects as well as carcinogenicity also. Among other techniques of pollutant removal, the adsorption method seems to be an effective and efficient treatment method due to simplicity of design, recycling of adsorbent, economic feasibility, and nonexistence of harmful residues. Various conventional adsorbent such as zeolites, activated carbon, activated alumina, clay etc. have been used for the pollutant remediation but these adsorbents are neither economically viable nor very efficient and showed very low adsorption capacity.

In the past few years, the nanoadsorbents have showed superior adsorption capacity due to its high surface area and presence of requisite functional groups. Graphene and its derivatives among other carbon nanomaterials have gained more attention due to their unique physiochemical properties. Graphene oxide is a functionalized form of the graphene which contains various oxygen functional group on its surface as well as showed high surface area and these properties makes it promising adsorbent for metal ions.

The background information and the literature review revealed that many conventional adsorbent have been reported for the adsorptive removal of pollutant species but the use of graphene based nanoadsorbent for the removal of fluoride and lead ions has not much explored yet. Thus, an attempt has been made to utilize graphene oxide derived nanocomposites for the effective removal of fluoride and lead from water due to their exceptional high adsorption capacity and possibility of regeneration and reuse of the exhausted adsorbent.

The materials and different experimental procedure used in the present investigation are given in chapter second. The details of batch and column experimentation, standard solution preparation, analysis method of metal ion also given in this section. The various analytical technique i.e. Surface area measurement (BET), pHzpc, Scanning Electron Microscopy (SEM) Analysis, Energy Dispersive X-ray Analysis (EDX), X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), Raman were used to characterized the prepared adsorbent. This section also outline the detailed discussion on the different mathematical models used for batch as well as column adsorption experiment studies.

The third chapter is devoted to the batch mode remediation of the fluoride by GO/ZrO<sub>2</sub> nanocomposite. The nanocomposite was prepared by simple hydrothermal method in which GO and ZrOCl<sub>2</sub>.8H<sub>2</sub>O were taken as the starting materials. The effect of various process parameters such as pH, adsorbent dose, metal concentration, and temperature on the uptake of fluoride by rGO/ZrO<sub>2</sub> has been evaluated. The prepared nanocomposite showed high surface area and extraordinary adsorption capacity for the removal of fluoride from water. The pHzpc of the rGO/ZrO<sub>2</sub> nanocomposite was found to be 7.3. The maximum uptake capacity of rGO/ZrO<sub>2</sub> was found to be 46 mg/g at initial fluoride concentration of 25 mg/L, rGO/ZrO<sub>2</sub> dose 0.5 g/L, temperature 30°C, and pH 7. The establishment of equilibrium of fluoride removal within 50 min suggested that the current adsorption system was faster. The kinetics of the current adsorption system indicated that the adsorption process followed pseudo-second-order kinetic model which is in accordance with the above result. The external mass transfer studies has given the value of coefficient of mass transfer ( $\beta_t$ ) which is high enough to ensure the rapid removal of the fluoride by adsorption process. The application of intraparticle diffusion model and Richenberg model indicated that the adsorption process was governed by intraparticle diffusion along with external diffusion. The equilibrium data fitted well with Langmuir isotherm which confirmed that the adsorption of fluoride was monolayer. The values of mean adsorption energy (E kJ/mol) calculated from D-R isotherm model was observed in the range of 8-16 kJ/mol which suggested the chemisorption nature of the fluoride removal. The negative values of  $\Delta G^0$  recommended the spontaneity of the process whereas the positive value of  $\Delta H^0$  suggested the endothermic process for the fluoride adsorption. The batch mode results concluded that the rGO/ZrO<sub>2</sub> would be a potential adsorbent for fluoride removal from the water at ambient condition i.e. 30°C temperature and neutral pH. These obtained

results will be helpful to design the up-flow continuous column for the treatment of fluoride contaminated water.

The practical applicability of fluoride ion removal by rGO/ZrO<sub>2</sub> nanocomposite was tested by continuous up-flow fixed-bed column system and has been reported in chapter four. The performance of the column was evaluated in terms of breakthrough curves. The effect of various column parameters (bed height, flow rate, and initial fluoride concentration) on the column adsorption performance has been evaluated. It was revealed from the results that the uptake capacity increased as the bed height increased which improved the adsorption performance while, uptake capacity was decreased with the increase in flow rate. The increase in uptake capacity was also observed with increases in initial fluoride concentration. The maximum uptake capacity was found to be 44.7 mg/g at bed height of 7.5 cm (initial concentration of 25 mg/L and flow rate of 1.66 mL/min). The BDST model was used to establish the relationship between service time ( $t$ ) and bed height ( $Z$ ) and the experimental data was found to be best fitted to this model. The BDST model was also applied for predicting the design parameters of flow rate of 3.32 mL/min from the 1.66 mL/min flow rate of sample. The experimental data was also applied to the Thomas and Yoon–Nelson model for describing the fixed bed adsorption system. The 10% NaOH solution was used to study the adsorption performance for three adsorption-desorption cycles of the rGO/ZrO<sub>2</sub> for fluoride ion removal and adsorption capacity was observed to be good for all the three cycles. The result of adsorption column life factor indicated that the adsorbent bed predicted to have sufficient bed capacity to avoid the breakthrough at time  $t = 0$  for up to 15.11 cycles.

The efficacy of the GO/MgO nanocomposite for the adsorptive remediation of the lead ion from water was studied by batch system which is presented in chapter five. The nanocomposite i.e. GO/MgO showed remarkable high adsorption capacity of 190 mg/g at ambient pH (6.5) and temperature (30°C). The pH of potable water usually lies in between 6 to 7. Therefore, the GO/MgO can be utilized for the removal of lead ion from the drinking water without making large alteration in pH and temperature of water. The pHzpc of the GO/MgO nanocomposite was found to be 6.0. The uptake capacity was higher in contrast to other previously reported adsorbents and the equilibrium was established in the very short period of time i.e. 30 min. The kinetic study of lead ion adsorption on the GO/MgO was also in support of the above fact because the pseudo-second-order kinetic model of adsorption fitted well with the experimental data. The external mass transfer and Weber-Morris model finding revealed that the intraparticle diffusion along with external mass transfer was actively participating in the rate controlling step. The Boyd kinetic model also indicated the involvement of intraparticle diffusion process in the rate controlling step. This adsorption system well followed the Langmuir isotherm model which was indicated by high  $R^2$  values and suggested the monolayered adsorption. The D-R isotherm model recommended that the adsorption was chemical in nature. The thermodynamic studies suggested that the adsorption was endothermic and spontaneous in nature. The thermodynamic and isotherms studies indicated that the optimum temperature for the adsorption of lead by GO/MgO was 30°C which was ambient temperature. Thus, the present adsorption process was inexpensive and energy saving. The data generated by kinetics, isotherms, and thermodynamics studies from the batch experimentation will be useful for the of the continuous column for the fabrication of treatment plant for lead

removal. The present system thus may be valuable for the formation of adsorbents in future which showed excellent adsorption capacity.

Chapter six deals with the remediation of lead ion by GO/MgO nanocomposite in continuous up-flow fixed-bed column system. This study deals with the adsorption performance of the column for the removal of toxic lead ions from aqueous in terms of breakthrough curves. The adsorption performance of lead was strongly affected by variation in inlet lead ion concentration, flow rates as well as bed height. The adsorption performance of the column improved with increase in bed height whereas, decreased with increase in flow rate. However, the column uptake increased with increase in inlet lead concentration. The maximum uptake was found to be 187.9 mg/g at flow rate of 1.66 mL/min and 7.5 cm of bed height. The BDST model was successfully applied in order to predict the relation between service time and bed height which was important to design the column. The BDST model was also utilized for prediction of column parameters to design new column for the flow rate of 4.98 mL/min from a sample flow rate of 1.66 mL/min. The experimental kinetic data successfully applied to the mathematical models i.e. Thomas and Yoon-Nelson models which were well fitted to these models and the studies were useful for application of the large scale field application. The column was regenerated with the 0.1M HCl solution and the adsorption performance was evaluated up to the three adsorption-desorption cycle. The column adsorption life factor predicted the life of the adsorbent and for this case the adsorbent was anticipated to have enough capacity to avoid the breakthrough at time  $t=0$  for up to 6.7 cycles and it was also predicted that the bed would be completely exhausted (zero uptake) after 17.3 cycles.