

Water is the most vital natural resource which is essential for sustaining all type of life form on the earth. It is estimated that the groundwater contributes only 0.6% of the total water resources on earth. It is the primary and preferred source of drinking water in rural as well as urban areas, particularly in developing countries. In the past few years, the economical growth steady up leads to urbanization, industrialization as well as due to geogenic sources the groundwater is getting polluted and become unsafe for consumption. The pollution of water due to the release of the cationic and anionic pollutant into ecosystem has become a global concern. These species can enter natural waters resources through release of wastewater, industrial activities, and domestic effluents. Ingestion of these pollutants by the human being caused severe developmental and neurological disorders over relatively short periods of time or even death. [Ray and Shipley (2015), Harrison (2005), Islam and Patel (2011)]. Therefore, the efficient removal of these pollutants from water up to its permissible limit is necessary in order to protect the entire ecosystem to become contaminated as well as it will inhibit the transfer of these ions into the food chain [Madadrang *et al.* (2012)].

Lead [Pb(II)] ion is one of the toxic metal ion which introduces in water by mineral dissolution, precipitation, and sorption/desorption of chemical species as well as by runoff from various chemical industries such as metal plating facilities, battery manufacturing, fertilizer, mining, paper and pesticides, metallurgical, mining, fossil fuel, tannery. Lead ion is a non-biodegradable hazardous heavy metal that easily accumulates in the human body. The primary source of lead in the human body is the drinking water, containing a substantial amount of lead ion. Initially, it can enter the body through the digestive tract and lungs and spread by the blood throughout the body. Presence of large quantity of lead ion in drinking water will cause anaemia, cancer, renal kidney disease, nervous system damage and mental retardation .

Fluoride ( $F^-$ ) ion contamination in groundwater has been recognized as one of the serious problem worldwide. Fluorides ion in drinking water may be beneficial or detrimental depending on their concentration and total amount ingested. Fluoride ion is beneficial especially to young children for calcification of dental enamel when present within the recommended limit (1.0-1.5 mg/L). An excess of fluoride ion in drinking water, causes dental fluorosis and skeletal fluorosis. In addition to Lead, Arsenic, and Nitrate ions the World Health Organization (WHO) classified the fluoride ion as one of the dangerous contaminant of the water causing large scale deleterious effects on human health. The groundwater is the major source of fluoride toxicity which is polluted by dissolution of rocks and minerals containing fluorine. Therefore researchers of all over the world paid attention to the need of discover an effective efficient and economical technology for the excess removal of these pollutant ions from water. Among various available water treatment technologies, adsorption process is considered better because of convenience, ease to handle, simplicity in design and cheap in operation.

In the past, many conventional adsorbents have been used by various researchers for the removal of these pollutants from water which includes activated carbon, agricultural products, natural materials, or microbial and non-microbial biomass which were used as most preferred adsorbent [Kurniawan *et al.* (2006), Ahmaruzzaman (2008)]. However, these adsorbent contain various demerits such as disposal problems, poor mechanical stability, and lower uptake capacity and thus they cannot be applied for industrial application [Chowdhury and Balasubramanian, (2014)].

In the past few years, the scientist from all over the world paid attention to the nanoscale materials due to their unique physiochemical properties and have been applied in many research field. Among different adsorbents, carbon based adsorbents

receive much attention than other adsorbents because of its simplicity, mass scale availability, and environmentally benign nature.

In the last decade, carbon based nanoadsorbent i.e. carbon nanotubes (CNTs), have used for removal of many inorganic and organic pollutant species due to their unique physical and chemical properties and nanoscale size [Upadhyayula *et al.* (2009), Ren *et al.* (2011)].

In the current scenario, graphene emerges as ‘wonder material’ showing the application in various field as we all considered as a promising adsorbent in the field of water purification [Liu *et al.* (2012)]. Graphene is two-dimensional,  $sp^2$  hybridized carbon network with a honeycomb crystal structure having high specific surface area and can be prepared by economical and simple chemical oxidation– exfoliation– reduction method [Ai *et al.* (2011)]. Graphene oxide (GO) is the important derivative of the graphene which is functionalized by various types of oxygen functional groups such as carboxyl (-COOH) and carbonyl (-C=O) groups at the sheet edges and epoxy (C-O-C) and hydroxyl (-OH) groups on the basal plane. The key importance of graphene oxide attributed due to its high surface area, the presence of abundant oxygen functional group and easy water dispersibility The graphene-based nanocomposites showed increased sensitivity, selectivity and detection limit for pollutants which opens up the new path to apply these materials for large-scale wastewater treatment .

Adsorption experiments were performed initially in batch mode by optimizing one parameter at a time approach. In this process, the effect of one parameter was investigated on the adsorption performance while other parameters were kept constant. Furthermore, adsorption performance was also examined with the help of fixed up flow column experiments to verify its applicability at large scale applications. Thus the

present study mainly aimed to synthesized the suitable adsorbent and cheap methods for the treatment of water/wastewater.

### **Thesis Organization**

The experimental work and results are summarized in the thesis in the six chapters as follows:

**Chapter I:** consist of the introduction and literature review. This section also focus on the various other remediation methods including adsorption process. The importance of adsorption process and approaches was also reviewed.

**Chapter II:** This section covers the materials and method used for this study. This chapter also includes the detailed spectroscopic characterization of the adsorbent. Various mathematical models related to the batch and fixed bed continuous experiments of this adsorption system are also discussed in this chapter.

**Chapter III:** This chapter comprises the removal of fluoride ion by rGO/ZrO<sub>2</sub> nanocomposite in batch mode and examining the effect of pH, rGO/ZrO<sub>2</sub> dose, temperature, initial fluoride ion concentration and contact time on the uptake capacity of the rGO/ZrO<sub>2</sub> nanocomposite. Furthermore, isotherm, kinetic and thermodynamic studied are also carried out to understand the nature of the adsorption and to enumerate the order and rate controlling step of the adsorption process

**Chapter IV:** This chapter deals with the application of rGO/ZrO<sub>2</sub> nanocomposite in the continuous up-flow fixed bed continuous column method for the remediation of fluoride ion. The experiments were also conducted at different bed height, effluent flow rate and initial fluoride ion concentration to examine their effect on adsorption

capacity. Further Bed depth service time (BDST) model, Thomas model and Yoon-Nelson model are also investigated for the modeling and prediction of process design.

**Chapter V:** This section contains the detailed batch experiment involving removal of lead by Graphene oxide/MgO nanocomposite. The effect of various variables i.e. pH, GO/MgO dose, temperature, initial lead ion concentration and contact time on the uptake capacity was studied along with isotherm, kinetic and thermodynamic studies.

**Chapter VI:** This chapter covers the studies of removal of lead ion by GO/MgO nanocomposite in fixed-bed up-flow continuous column mode. The effect of various column parameters, i.e. bed height, effluent flow rate and initial lead ion concentration on the column performance were also examined. Moreover, various mathematical models are also applied to describe and analyze the breakthrough curve.

In the last Summary is given which consists of all the important results of each chapter. The recommendations and future prospects are also included in this chapter. In the end, references are listed which are cited during this whole work along with the authors' publications.