Summary

The thesis entitled **"Synthesis, Characterization and Application of Nano-Adsorbents for Removal of Metallic Species from Aqueous Solutions"** personified the synthesis of nano-adsorbents namely, nano-alumina (n-Al_2O_3) and nano-cupric oxide (n-CuO) to accomplish removal of metallic species such as chromium, Cr(VI) and nickel, Ni(II) from aqueous solutions. Water is one of the most important of all natural resources sustaining life on the Earth and making it a green planet. So, it can be said that it is an "Elixir of life." However, environmental pollution in terms of water pollution is becoming one of the most serious problems of the day, which causes detrimental effect to humanity and other life forms. Industrialization and anthropogenic activities for a better quality of life have always resulted in some impact on the environment and thus, the planet has experienced an assortment of pressing environmental challenges such as climate change/global warming, extreme era of waste, and water pollution, leading to serious environmental degradation and contributes a major share to the overall imbalance of the ecosystem. Among the numerous contaminants found in water, heavy metals require special attention because of their high chemical toxicity, bio-accumulative effect, inability for self-purification, easy migration and transformation causing both short and long term adverse effects, even at trace concentrations.

During recent years, the adsorption process has come on forefront as one of the major techniques, especially for removing pollutants from dilute solutions. In this sense, new adsorbents based on nanomaterials are being extensively explored. In the last years, the development of new, efficient and low cost nanomaterials for their application in

treatment of water/wastewater has been of great interest due to their striking properties such as large surface area, low dose requirement, high reactivity and strong adsorption. Keeping these views in mind, the present investigations are oriented towards the removal of chromium and nickel from aqueous solution by adsorption technique using various adsorbents (nano-alumina and nano-cupric oxide). In order to understand the mechanism of adsorption and interactions at solid-solution interface, various relevant experimental parameters such as effect of initial concentration, contact time, adsorbent dose and pH of the adsorptive solution have been studied along with the desorption of pre-adsorbed species.

All experiments were designed via Response surface methodology (RSM) as the conventional and classical methods of studying a process by maintaining other factors involved at an unspecified constant level does not depict the combined effect of all the factors involved. The limitations of a classical method such as time consuming, protracted, labour-intensive and requires a number of experiments to determine optimum levels, can be eliminated by optimizing all the affecting parameters collectively by statistical experimental design such as response surface methodology (RSM). The application of statistical experimental design techniques in sorption processes could result in improved product yields, reduced process variability, closer confirmation of the output response to nominal and targeted requirements, as well as reduced development time and overall costs. Box-Behnken (BBD) of is a good design of RSM because it is slightly more efficient than the central composite design but much more efficient than the three-level full factorial designs in terms of cost when the number of factor is higher than 2. Another advantage of BBD lies in the fact that it does not contain combinations for which all factors are simultaneously at their highest or lowest levels. Thus, it is useful in averting unnecessary experiments performed under extreme conditions that may result in unsatisfactory outcomes. These features incited our group for adopting BBD, RSM for this present study.

In order to assess the best process for determination of kinetic and isotherm parameters, isotherm and kinetic data were analysed by linear and non-linear methods. In recent years, linear regression for the best fitting of isotherm and kinetic data has been one of the most feasible tools for the mathematical analysis of adsorption systems. But due to inherent biasness associated with it, and also its inappropriateness for isotherms with more than two parameters, alternative isotherm parameter sets were determined by non-linear regression. Linear methods include the fitting of the data in the linear isotherm and kinetic equations whereas, non-linear methods include the use of curve fitting using Origin along with fitting to the non-linear isotherm and kinetic equations. Non-linear curve fitting for isotherm and kinetic parameter determination using Microcal origin was done by customizing a non-linear function for isotherm and kinetic model where parameter initialization is taken as 1.

This thesis is systematically organized based on the synthesis, characterization of the synthesized nano-adsorbents and their application in the removal of metallic species from aqueous solutions. The chapter wise summary of the thesis is described below.

Chapter 1 deals with the Introduction about environmental pollution in terms of water pollution, availability of water, various types of pollutants responsible for water pollution and numerous methods of wastewater treatment along with their advantages and disadvantages. The emergence of nanotechnology-enabled water and waste-water treatment that involve highly efficient, modular and multi-functional processes to provide high performance, affordable water and wastewater treatment solutions that less rely on large infrastructures is also discussed in this section. Nanomaterials possessing novel size-dependent properties different from their large counterparts are being continuously explored for water treatment and their strategies of preparation has been also elucidated in this section. It also narrates my own research efforts, rationale and ideas behind the synthesis of some nano-adsorbents and their potential use as adsorptive media.

Chapter 2 provides an overview of various nanomaterials employed for the treatment of metal bearing water and waste-water by several scientific workers based on pertinent literature survey. An attempt has been made to make an up-to-date survey of the literature in the area related to the research in the thesis.

Chapter 3 embodies information regarding various materials used for experimentation, adsorbates and adsorbents, analytical instruments for characterization of adsorbents, and methods involved all through the research work.

Chapter 4 provides an insight into detailed description of synthetic procedure adopted for synthesis of nanomaterials used as adsorbents and also explores their physico-chemical properties with the aid of sophisticated analytical instruments. The synthesized materials exhibit nanoscale dimensions examined by TEM and SEM micrographs also the amorphous architectures are scrutinized by X-ray diffraction and SAED pattern corresponding to TEM images. FTIR spectral analysis identifies the functional groups characteristics of the materials, that are supposed to be responsible for adsorption of metallic species.

Chapter 5 demonstrates the employment of Box-Behnken design of RSM as an experimental tool to explain the effect of main operational parameters and their interactions for determining the conditions leading to high Cr(VI) uptake efficiency using alumina nanoparticles. An optimum condition for chromium uptake was achieved with RSM at initial chromium ion concentration of 5 ppm, pH 2.03 and adsorbent dose of 20g/L for achieving 94% removal with desirability value of 1. The time of equilibrium was 60 min. The isotherm data obtained for the system followed Langmuir model and kinetics was best elaborated by pseudo-second-order model. Among linear and non-linear analyses for isotherm and kinetic parameter determination, linear analysis was found more appropriate on the basis of high value of determination coefficient. The overall process was feasible, exothermic in nature with positive value of entropy. The experimental results showed that under optimized conditions, nano-alumina can be used as an adsorbent for the removal of Cr(VI) from aqueous solutions.

Chapter 6 investigates Ni(II) adsorption on γ-alumina nano-adsorbent using RSM techniques under BBD statistical design. Among various operational parameters such as pH, adsorbent dose and initial concentration, pH of solution has pronounced effect on removal followed by adsorbent dose and initial concentration. Equilibrium time was found 7 min for adsorption. The adsorptive removal of Ni(II) was endothermic, feasible and spontaneous in nature. Under the conditions predicted by the model, the optimum result can be achieved at pH 7.0, initial concentration 25ppm and adsorbent dose 20 g/L. Linear approach of kinetic and isotherm determination best explained the data. Pseudo-second-order kinetic and Langmuir isotherm models best fitted to the adsorption data. The experimental results depicted that under optimized conditions, γ-alumina can be used as a potential candidate for treatment of industrial effluents containing nickel ions.

Chapter 7 deals with the application of nano-cupric oxide for removal of Cr(VI) from aqueous solutions. The optimum conditions for achieving the optimum results as predicted by model were initial concentration 5ppm, pH 2.0 and adsorbent dose 18.84 g/L. The experimental parameters were optimized for the optimum response. The adsorption equilibrium data was well fitted to Freundlich isotherm model and the kinetics of was well explained through pseudo-second-order kinetic model. The overall process was feasible, spontaneous and exothermic. Linear approach for analysing the isotherm as well as kinetic parameters was found more appropriate than the non-linear approach. The adsorbent was successfully regenerated and reused upto five consecutive cycles without significant loss in removal capacity. The experimental results exhibited that cupric oxide nanoparticles can be a good alternative for Cr(VI) removal from aqueous solutions.

Chapter 8 highlights adsorptive removal of Ni(II) over cupric oxide nanoparticles from aqueous solutions was modelled via Response Surface Methodological approach. pH of the solution was found to be most influential parameters among various other operational parameters. Under the specified conditions predicted by the model, 100% removal can be achieved at pH 7.0, initial concentration 25ppm and adsorbent dose 18.8g/L. Increased removal with rise in temperature confirmed the endothermic nature of the adsorption process. Equilibrium was achieved within 30 min of adsorption. The adsorption equilibrium data was best interpreted by Langmuir isotherm model and adsorption kinetics followed pseudo-second order model. Intra-particle diffusion was not the only rate-controlling step. Boyd model proposed the involvement of film diffusion as a rate controlling step in the process. Furthermore, linear method of analysis was most appropriate than non-linear analysis for determination of isotherm and kinetic parameters. The experimental findings concluded that under optimized conditions, cupric oxide can be used as an effective adsorbent for treatment of industrial effluents containing nickel ions.