Chapter-8

Conclusions and Future Scope

This chapter reports the conclusive remark on the role of synthesis method on the electro-kinetic properties of magnetic nanoparticles in the presence of different inorganic electrolytes. It also reports the conclusion of adsorption analysis of BSA and HS onto the NiFe$_2$O$_4$ nanoparticles synthesized by DC thermal plasma route. Hence, this chapter concludes the main contribution of research work carried out in this thesis and the future scope in order to explore this new technique of synthesis for the magnetic separation of various organic and biomolecules.
8.1 Summary and Conclusions

The main contribution of research work carried out in this thesis is summarized here. The magnetic nanoparticles of NiFe$_2$O$_4$ and CoFe$_2$O$_4$ were synthesized by chemical co-precipitation and dc thermal plasma route. The systematic study of electro-kinetic properties of these nanoparticles in the presence of different inorganic electrolytes is carried out for two different types of particles. The zeta potential and hydrodynamic particle size was determined by using zeta potential analyzer. The micro-structural analysis was done using FESEM, TEM and HRTEM. The nanoparticles of NFOTP were successfully functionalized with polymethacrylic acid (PMAA) by self-emulsion polymerization technique. The coating of nanoparticles was essential done in order to enhance the adsorption capacity and selectivity of target molecules. It was observed that due to effective functionalization of NFOTP with polymers the physico-chemical properties were completely changed. Moreover, the systematic adsorption analysis of Bovine Serum Albumin (BSA) and Humic Substances (HS) onto the NiFe$_2$O$_4$ nanoparticles was carried out in order to determine its applicability in the magnetic separation technique. The analysis of adsorption kinetics was carried out with the help of pseudo-first order, pseudo-second order and intra-particle diffusion model. Moreover, the analysis of adsorption isotherms was carried out with the help of Langmuir, Freundlich and Temkin models. The comparison of fitting of data to linear and non-linear kinetic and isotherm equations was carried out in order to determine the best fit. Thus, the conclusions drawn from each experimental work carried out in this thesis are briefly summarized below.

The highly crystalline nanoparticles of NiFe$_2$O$_4$ and CoFe$_2$O$_4$ were synthesized by DC thermal plasma route at different optimized plasma parameters. The magnetic nanoparticles were also synthesized by chemical co-precipitation route at different calcination temperature. High values of zeta potential are observed for both the magnetic nanoparticles synthesized by dc thermal plasma route as compared to chemical route. The maximum zeta potential value of +63mv and –58mv was obtained at pH 3.64 and 9.66 respectively for NFOTP synthesized at 500 Torr and 6 kW of plasma parameters. It was observed that the magnitude of zeta potential increases with increase in calcination temperature. The maximum zeta potential value of + 40mv and - 42mv was obtained at pH 3.64 and 9.66 respectively for particles calcined at 800°C. Similar results were obtained for CFOTP and CFOCP nanoparticles. The
iso-electric point of NFOTP and CFOTP was obtained at pH 7.25 and pH 7.10 respectively. This high value of zeta potential is attributed to the steep temperature gradient involved during the synthesis process which produces highly crystalline nanoparticles with large surface defects. The electro-kinetic properties were found to be very sensitive to the heterogeneity of the oxide surfaces together with the surface topology. No effect of plasma parameters was observed on the electro-kinetic properties of magnetic nanoparticles. However, increase in the zeta potential values and iso-electric point is observed with increase in the calcination temperature in case of chemically synthesized nanoparticles. Substantial effect of electrolytes was found on the electro-kinetic properties of nanoparticles. It was observed that the maximum value of zeta potential was obtained for NaNO₃, whereas, the ions of CaCl₂ and Na₂SO₄ result in the reduction of the zeta potential for both the particles. The Na₂SO₄ and CaCl₂ electrolytes are found to decrease the magnitude of zeta potential because these are 2:1 type of electrolytes which results in the compression of EDL. Also sulfates provide better neutralization effect than chloride ions causing more reduction in the zeta potential values. It was also observed that the presence of different electrolytes does not affect the iso-electric point of both the nanoparticles. The inorganic ions are observed to screen the electrostatic repulsive force between the charged particles in the solution thus enhancing the short range van-der Waals interactions which promotes the rate of agglomeration. It was observed that the zeta potential decreases with increase in the ionic strength of the colloidal solution. At higher concentrations, the decay constant is faster which results in the smaller double layer thickness. Higher agglomeration results in the decrease of optical absorbance which is found to be in analogous with the results obtained for the zeta potential. The NiFe₂O₄ was chosen as the adsorbent for further due to its high saturation magnetization and for being soft magnetic material.

Micro-structural analysis suggests that the method of synthesis affects the physico-chemical properties of NiFe₂O₄ nanoparticles. It is observed that the NFOTP particles are non-agglomerated in nature and possess sharp boundaries with high crystallinity as compared to NFOCP particles. The NFOTP particles are found to have higher surface roughness, saturation magnetization and surface defects making them more reactive as compared to NFOCP. The higher value of saturation magnetization for NFOTP was attributed to the wider particle size distribution and high crystallinity which is expected in high temperature thermal
plasma synthesis process. The RMS surface roughness obtained for NFOTP and NFOCP nanoparticles was 8.94 nm and 4.10 nm respectively. The highly resolved image of NFOTP show clear faceted surfaces with sharp boundaries where most of the smaller particles exhibit hexagonal faceting whereas the larger ones exhibit square or rounded facets. However, the surface of NFOCP was seen to be very hazy, probably indicating an amorphous layer. The adsorption of BSA onto NFO nanoparticles increases with increasing pH from 3.64 attains a maximum at pH value of 5.58 and decreases with further increase in pH values.

The NFOTP had higher adsorption capacity than NFOCP for all the pH values under study. The maximum adsorption (231.57µg/mg) of BSA at 37°C was observed at pH value of 5.58 for thermal plasma synthesized particles than those synthesized by wet chemical means (178.71µg/mg). Higher adsorption of BSA onto NFOTP than that of NFOCP is due to the dependence of adsorption on protein properties as well as surface properties of the material like surface charge, surface energy, polarity and morphology. The adsorption analysis confirms the fitting of experimental data to Langmuir model than to the Freundlich model. This suggests that there is higher probability of formation of monolayer onto the surface of NiFe₂O₄ nanoparticles.

The NiFe₂O₄ nanoparticles synthesized by dc thermal plasma route were effectively functionalized with PMAA polymer using self-emulsion method. The saturation magnetization of NiFe₂O₄ nanoparticles was reduced from 46.53 emu/gm to 39.21 emu/gm due to effective functionalization of NiFe₂O₄ nanoparticles with PMAA polymer. The FTIR confirms the effective functionalization of PMAA where the core particle (NFOTP) retains its original properties. The isoelectric point for PMAA functionalized particles shows remarkable shift from 7.25 to less than 2.82. Moreover, the PMAA functionalized NiFe₂O₄ nanoparticles possesses negative values of zeta potential for all the pH values in the measurement range. Bare NiFe₂O₄ nanoparticles satisfies pseudo-first order kinetic model for initial 25 min of adsorption and later on pseudo-second order kinetic model is satisfied. However, PMAA functionalized nanoparticles satisfies pseudo-first order kinetics for initial 20 min of adsorption. The intra-particle diffusion model reveals that the regression does not pass through the origin and therefore particle diffusion is not the only rate controlling step for both the particles. Moreover, pore diffusion is faster in case of PMAA functionalized particles as compared with bare NiFe₂O₄ nanoparticles. Adsorption equilibrium is reached at
lower concentrations of BSA in case of bare NiFe$_2$O$_4$ particles than for PMAA functionalized NiFe$_2$O$_4$ nanoparticles. PMAA functionalized NiFe$_2$O$_4$ nanoparticles has higher adsorption capacity for BSA. Bare NiFe$_2$O$_4$ nanoparticles satisfy Langmuir adsorption isotherm whereas PMAA functionalized particles satisfies Freundlich adsorption isotherm.

The NFOTP nanoparticles synthesized at 500Torr and 6kW of DC power were found to have high adsorption capacity for Humic Substance (HS) molecules from the suspensions. It was observed that there was small reduction in the saturation magnetization of HS-NFOTP composite and is due to the effective coating of non-magnetic HS. However, there is not much reduction in the magnetic properties of NiFe$_2$O$_4$ after the adsorption of humic substances which therefore remains effective in the removal of HS-NFOTP composite by external magnetic field. The observed weight loss in TGA analysis shows the effective binding of HS onto NFOTP nanoparticles. It can be observed that initially there is rapid increase in the adsorption of HS and the adsorption attains saturation after certain time period for all the HS concentrations under study. Moreover, less time is required to reach the saturation with increase in the HS concentration due to increase in the driving force. Here the comparison of fitting of experimental data to non-linear and linear forms of equation was carried out. The linear fitting of kinetic model equations suggest that pseudo-first order model is satisfied for initial 35 min of adsorption whereas pseudo-second order is satisfied for the entire adsorption process. The non-linear fitting of adsorption kinetic models suggests that the pseudo-first order (PFO) kinetic model is satisfied for the entire adsorption process. Here the linear method failed to predict the accurate value of $q_e$. This is because the linear fitting of experimental data just verifies the hypothesis of linear regression instead of verifying the theory of adsorption kinetics. The intra-particle diffusion model suggests that the whole adsorption process is multi-linear. The linear and non-linear fitting of adsorption isotherms suggests that Langmuir isotherm fits better than the Freundlich isotherm suggesting the monolayer coverage of HS onto NFOTP surfaces. This study shows that the fitting of non-linear forms of adsorption equations is superior to the linear forms. The different results obtained by linearizing the kinetic equations are due to the addition of variation in the error structure developed by linearizing the non-linear equation. The distribution of error may vary depending upon the way the kinetic equation is linearized. Here some of the assumptions behind linear regression are violated. Therefore, fitting of
experimental data by non-linear method must be adopted to obtain the correct adsorption parameters. There is decrease in the amount of HS adsorbed with increase in pH values due to decrease in the electrostatic interaction between the HS and NFOTP particles. From FTIR spectrum it can be concluded that the functional groups of HS were responsible for its ligand exchange with NFOTP particles.

Moreover, important parameters like morphology, crystallinity, surface defects, surface charge and state of agglomeration is found to have significant effect on the antibacterial activity and field emission properties of NiFe$_2$O$_4$ nanoparticles. The NFOTP particles showed significant antibacterial activity against E.coli. These results are important in understanding its implications in toxicological studies, which is still limited for particles synthesized by gas phase condensation method.
8.2 Future Scope

The results and conclusions drawn from this work reveal that the magnetic nanoparticles synthesized by DC thermal plasma route have high colloidal stability and can be effectively used in various fields of engineering and biotechnology. The thermal plasma route can be used to synthesize nanophase multi-component systems which can further play an important role in various industrial applications. The future development in the adsorption science is a major challenge because of its advantages like low cost, reusable capability of adsorbents and capability in manufacturing new and novel materials with specific properties. However, the perspective of adsorption can only be shaped by developing the relationship between theories, experiments and practice. Therefore, special attention must be given to the advancement of new theories stimulated by modern techniques. There is need to develop nano-adsorbents with specific functional groups which can enhance the specificity and capacity of adsorption. The development of such adsorbents is still a challenge in the nano-industry. Also there is need to develop hybrid processes where the adsorption, filtration, chromatography etc. are combined to achieve the required bio-separation goals. These hybrid methods are very promising for bio-adsorption processes. Also lot of development is expected in understanding the equilibrium and transport phenomena of fluids in materials. This is possible by using sophisticated simulation and modelling techniques which will reduce the gap between the microscopic and macroscopic worlds.