ABSTRACT

Life on planet earth depends on various natural resources and one such major resource is water. Water pollution is a major environmental issue faced by the modern world, which leads to ecological disequilibrium which can cause harmful effect on flora and fauna of the ecosystem. Pollution of water by heavy metals beyond a permissible limit is considered a threat due to their immense toxicity and their non-biodegradability. The purpose of wastewater treatment is to remediate polluted water and to reuse it within acceptable quality standards. Adsorption is a promising method for the removal of metal ions from wastewater because of its high efficiency, ease of handling and abundant availability of different classes of adsorbents. In the past few years, polymeric adsorbents have been emerging as a potential alternative to other adsorbents in terms of their vast surface area, perfect mechanical rigidity, adjustable surface chemistry, pore size distribution, selectivity towards heavy metal ions and feasible regeneration.

The aim of the present work is to synthesize 2-(p-chlorobenzalimino)terephthalic acid, 4,4’-bis(thiourea)biphenylsulphone (BTUBPS), 4-(N,N dimethylamino) benzalimino-2,5 dicarboxylic acid (DMABIDA) monomers through appropriate reactions and to ascertain their structures of monomers by FT-IR, $^1$H-NMR and $^{13}$C-NMR analyses. Polymeric resins Polyamide-I (PA-I), Polyamide-II (PA-II), Polyester-I (PE-I) and Polyester-II (PE-II) were synthesized from the above prepared monomers and then characterized by the FT-IR, $^1$H-NMR, $^{13}$C-NMR, SEM, EDX, TGA, XRD and DLS analyses. Among them, PA-I and PE-I were used as an adsorbents for the removal of Ni(II), Cd(II) and Zn(II) ions from
aqueous solution. Polymers, such as PA-II and PE-II were used for the adsorption of Hg(II) and Th(IV) ions from aqueous solution.

Parameters which affect the adsorption of metal ions such as, solution pH, adsorbent (resin) dosage, initial metal ion concentration, contact time and electrolyte were analyzed and optimized. Adsorption of metal ions onto the polymeric resin has been evaluated in terms of equilibrium, kinetics and thermodynamics studies. Data obtained from the studies on the effect of the initial metal ion concentration were fitted with adsorption isotherm models such as Langmuir, Freundlich, Sips and Temkin. Similarly, data obtained from the effect of contact time studies were fitted with kinetic models such as pseudo-first order, pseudo-second order and intraparticle diffusion. Thermodynamic parameters such as change in standard free energy change ($\Delta G^o$), enthalpy ($\Delta H^o$) and entropy ($\Delta S^o$) has been evaluated from data obtained from the effect of temperature studies.

Metal ions adsorbed PA-I, PE-I, PA-II and PE-II was characterized by FT-IR, SEM and EDX analyses to confirm the adsorption of metal ions on their surface. Ni(II), Cd(II) and Zn(II) ion concentrations in the aqueous solution before and after adsorption were determined using Atomic Absorption Spectroscopy (AAS). Concentrations of Hg(II) and Th(IV) before and after adsorption were determined spectrometrically by using UV-Visible spectrophotometer.

Studies on the effect of solution pH shows the maximum metal ion (Ni(II), Cd(II) and Zn(II)) removal was recorded at pH 6 for PA-I and PE-I. In case of PA-II and PE-II the maximum removal of Hg(II) and Th(IV) occurred at pH 5.
Percentage removal of metal ions increases with increase in adsorbent dose till a particular amount of adsorbent and thereafter remains constant, which may be due to the saturation of active sites on the adsorbent. In the present study, the maximum adsorption was attained with 20 mg dose of PA-I, PE-I, PA-II and PE-II.

The percentage removal of metal ions decreases with an increase in metal ion concentration. This is mainly due to the saturation of available active sites on the adsorbent. The application of isotherm models to the metal ion-adsorbent system indicates that both homogenous and heterogeneous surfaces exist under the experimental conditions studied. The Langmuir maximum monolayer adsorption capacity of the synthesized polymeric adsorbents was compared with other adsorbents which showed that PA-I, PE-I, PA-II and PE-II have higher adsorption capacity, when compared to other adsorbents.

Adsorption kinetics was found to be relatively fast and equilibrium was attained in 60 min. It can be seen that, the pseudo-second order model fits the adsorption process better than the pseudo-first and intraparticle diffusion kinetic models. External mass transfer controls the metal ion removal during the earlier stages of adsorption, and intraparticle diffusion during the later stages of adsorption.

The percentage removal of metal ions decreases with an increase in temperature. This is mainly due to the decrease in a surface activity suggesting that the adsorption of metal ion over the adsorbent is an exothermic process. The negative $\Delta G^\circ$ value indicates that the process is feasible and spontaneous in nature, negative $\Delta H^\circ$ value suggests the
exothermic nature of adsorption and $\Delta S^\circ$ can be used to describe the randomness at the adsorbent-solution interface during adsorption.

Studies on effect of electrolyte show that the percentage removal of metal ions decreases with increase in concentration of electrolyte (NaCl) from 0.05N to 0.5N. This is due to the fact that the presence of Na$^+$ ions from electrolyte competes with metal ions for the available adsorption sites on the polymer and hence reduction in percentage removal.

The maximum monolayer adsorption capacity values obtained from the multi-component system ($q_{\text{max}}^{\text{mix}}$) were less than those for the single-component solutions ($q_{\text{max}}$). The reason for this behavior is that one type of metal ion interferes with the uptake of other ions in the solution.

Aqueous solutions of 0.1N HCl, 0.1N HNO$_3$ and 0.1N CH$_3$COOH solutions are capable of eluting the metal ions from polymeric resins. Results show that both HCl and HNO$_3$ are equally good for desorption of metal ions. But the desorption efficiency of aqueous CH$_3$COOH is less, because of its weak acidic character. The regenerated polymers were used again for four adsorption cycles.

The overall results show that the newly synthesized chelating polymers bearing donor atoms are chemically resistant, thermally stable which serve as key contributory factors to exhibit high adsorption capacity towards all metal ions studied.