Summary
Summary

Very few chemical compounds present in the close human surroundings may be well thought out as beneficial to health. The majority of them functions detrimentally on humans even in minimal doses and occur in all of our environmental media – air, water and soil. One of the main culprits behind the widespread deterioration of environment is the material processing industries which produce and expel large amounts of waste effluents containing heavy metals into soil and water bodies. The pressure on industry to decrease emission of various pollutants into the environment is increasing due to governmental legislations. A wide choice of methods has been developed and is available to control and remove natural and anthropogenic pollutants. With regard to price–performance relation, adsorption technology is regarded as the most important technique to overcome the enduring degradation of environmental quality and thus plays a significant role both in environmental and human health control.

Adsorbents prepared by proper surface modification of lignocellulosic materials or commercial ion exchangers are capable of performing effectively in the treatment of metal containing effluents by lowering the effluent qualities in the order of ppb (µg/L) of residual metal/s. Ion exchange method is a ‘matured’ technology unlike sorption based on lignocellulosic materials which is in its infant stages. Modifications of ion exchangers with a view to incorporate new functionalities with predetermined aims are also in its early developmental stages. Advancements and improvements in performance of these types of materials
reduce costs and can thus become good candidates in the fight against toxic metals, intimidating our environment and health.

The use of banana stalk (BS), an abundantly available unused resource dumped as agrowaste in market places and agricultural farms, could be expected to be a technically viable and economically feasible precursor applicable for wastewater treatment, and most importantly, contribute to the sustainability of the surrounding environment. Leaching of organics restrict the possibility of using naive BS powder as adsorbent. In the present work, acrylamide was graft polymerized onto BS using ferrous ammonium sulphate/H$_2$O$_2$ redox initiator system in an aqueous medium. The effects of reaction variables, such as time, temperature and the concentration of monomer and initiator on the percentage grafting were studied with a view to judge the optimum parameters for maximum graft yield. A suitable mechanism involving the lignin of BS, which is considered to be more sensitive to polymerization due to the high concentration of $p$-hydroxyphenylpropane group as well as variable quantities of syringyl and guaiacyl groups, was suggested. The polymer grafted banana stalk (PGBS) thus obtained is suitably converted into an adsorbent with carboxylate functionality (PGBS-COOH) by treating with ethylenediamine in toluene, followed by refluxing with succinic anhydride in 1,4 dioxane.

FTIR spectra of BS and PGBS-COOH indicated the effect of surface modification by identification of proper peaks corresponding to the various functionalities and the polymeric backbone. The TG and DTA techniques highlighted the superior thermal stability associated with PGBS-COOH. XRD studies showed that on graft polymerization, a significant reduction in crystallinity took place due to some rearrangement in the morphology of cellulosic chains which in turn resulted in the loss of tensile strength of grafted chain and consequently enhanced the free mobility of grafted chain. The difference in surface
Summary

The adsorption characteristics of the newly developed adsorbent for the removal of toxic heavy metal ions like Pb(II), Co(II), Hg(II) and Cd(II) from aqueous solutions were studied in detail. The binding of metal ions by surface functional groups was strongly pH dependent. The adsorption of metals was found to decrease with decreasing pH because at low pH, the carboxylate functional groups would be more protonated and was less available to retain the metals. The dependence of metal uptake on pH suggests that the weak acidic carboxyl groups, R-COO\(^{-}\) of PGBS-COOH with pK\(_a\) range between 3.5 and 5.5 are the probable adsorption sites. A maximum adsorption of 95.8 and 85.4 % for Pb(II), 94.0 and 83.7 % for Co(II) and 91.3 and 78.0 % for Hg(II) occurred for an initial concentration of 50 and 100 mg/L respectively at a pH of 6.5. For Cd(II) a maximum adsorption of 89.1 and 79.8 % was observed at an initial concentration of 25 and 50 mg/L respectively. The pH\(_{pzc}\) of PGBS-COOH was found to be 5.5 and above this pH the surface charge of the adsorbent is negative. An ion exchange mechanism was also suggested for explaining the metal removal process. A comparative account of the adsorption of the same metals ions on naïve BS, revealed its comparatively lower adsorption ability. Adsorption of Pb(II), Co(II), Hg(II) and Cd(II) on PGBS-COOH studied at pH 6.5 decreased with increase in ionic strengths from 0.01 to 1.0 M NaCl at a fixed initial metal concentration of
Summary

50 mg/L. This is because electrostatic attraction plays an important role in the removal of metal ions by PGBS-COOH. When the adsorbent is in contact with the sorbate species in solution, they are surrounded by an electrical diffused double layer, the thickness of which is significantly expanded by the presence of electrolyte. Such expansion inhibits the adsorbent particles and metal ion species from approaching each other more closely and, though the decreased electrostatic attraction, leads to the decreased uptake of metal ions.

The adsorption data for the uptake of Pb(II), Co(II), Hg(II) and Cd(II) ions by PGBS-COOH with respect to change in contact time were studied for four different initial concentrations of each metal ions. The adsorption profile revealed that initially the adsorption is rapid due to the availability of sufficient number of exchange sites followed by a slow approach to equilibrium within 3h, due to saturation of adsorption sites. When the concentration of the solution was increased from 25 to 150 mg/L, the amount adsorbed increased from 12.43 (99.4 %) to 59.52 mg/g (79.37 %) for Pb(II), from 12.35 (98.8 %) to 56.47 mg/g (75.3 %) for Co(II), from 12.32 (98.5 %) to 51.89 mg/g (69.2 %) for Hg(II) and from 11.26 (90.1 %) to 46.34 mg/g (58.2 %) for Cd(II) respectively. The amount adsorbed on the PGBS-COOH at higher metal concentration is greater than the amount adsorbed at lower metal concentrations due to the increase in the driving force of the concentration gradient, on increase with initial concentration.

The rate constants of adsorption of metals from solutions were determined using the pseudo-first-order equation of Lagergren and pseudo-second-order equation of Ho and McKay. Lagergren plots were found to associate with low correlation coefficients but the correlation coefficients obtained for the pseudo-second-order lines were more than 0.989. A quantitative comparison of the two models using a normalized standard deviation Δq(%) reiterated the validity of the pseudo-second-order plots for all the metal ion adsorptions. For a decrease in the
initial metal ion concentration from 150 to 25 mg/L, the values of second-order rate constant, $k_2$ increased from $8.97 \times 10^{-3}$ to $1.35 \times 10^{-3}$ g/mg min for Pb(II), and from $2.23 \times 10^{-2}$ to $1.68 \times 10^{-3}$ g/mg min for Co(II), from $5.73 \times 10^{-3}$ to $1.23 \times 10^{-3}$ g/mg min for Hg(II) and $1.10 \times 10^{-2}$ to $2.48 \times 10^{-3}$ g/mg min for Cd(II). The linearised $k_2$ and $C_o$ values on a log–log plots were used to formulate equations to predict the rate constant of adsorption process, at any initial concentrations under similar experimental conditions.

The results obtained from batch adsorption experiments with varying the adsorbent dose between 1 and 10 g/L and initial Co(II) concentration between 150 and 600 mg/L at pH 6.5 and 30 °C on Co(II) removal were effectively used to develop a mathematical relationship to determine the percentage removal Co(II) at any time for a given initial Co(II) concentration and adsorbent dose. The relevance of the model was successfully tested under variable conditions like different initial Co(II) concentrations, varying adsorbent doses and at diverse pH values.

The pseudo-second-order kinetic model agreed very well with the dynamical behavior for the adsorption of metals on PGBS-COOH at different temperatures of 30, 40, 50 and 60 °C keeping 100 mg/L as the initial metal ion concentration. For an increase in temperature from 30 to 60 °C, the values of second-order rate constant, $k_2$ were found to increase from $2.01 \times 10^{-3}$ to $9.16 \times 10^{-3}$ g/mg min for Pb(II), and from $2.33 \times 10^{-2}$ to $9.13 \times 10^{-3}$ g/mg min for Co(II), from $1.81 \times 10^{-3}$ to $7.48 \times 10^{-3}$ g/mg min for Hg(II) and $3.58 \times 10^{-2}$ to $4.43 \times 10^{-3}$ g/mg min for Cd(II). On the contrary, the pseudo-first-order kinetic model fits the experimental data poorly for the entire range under study. This suggests that the rate-limiting step may be the chemical adsorption but not the mass transport. The increase in temperature favours the adsorption process by activating the adsorption sites and increases the chemical forces responsible for adsorption. The energy of activation
Summary

computed based on the Arrhenius equation were found to be 42.09, 39.03, 39.56 and 5.71 kJ/mol for Pb(II), Co(II), Hg(II) and Cd(II) respectively.

The analysis of the experimental sorption isotherm for four metal ions on PGBS-COOH at different temperatures from 30 to 60 °C showed that the adsorption is quite rapid at low initial concentration followed by a slow approach to equilibrium at high metal concentration. The isotherm curve obtained was of L-type nature of Giles classification which indicated strong tendency in the process of monolayer formation. The equilibrium data was tested for best among the Langmuir, Freundlich and Scatchard isotherm models.

The Langmuir plots of $C_e/q_e$ versus $C_e$ were found to be linear over the whole concentration range studied with high $r^2$ illustrated the applicability of Langmuir isotherm. The maximum adsorption capacity $Q^0$ which is a measure of the ability of the adsorbent was found to be 185.34 mg/g for Pb(II), 166.93 mg/g for Co(II), 137.89 mg/g for Hg(II) and 65.89 mg/g for Cd(II) at 30 °C. It was also observed that $Q^0$ values increased with increase in temperature which is advantageous since real wastewaters normally exist above room temperature. The variation in adsorption capacities of the sorbent for Pb, Hg and Cd at 30 °C were correlated to their hydrated ionic radii. Even though Co(II) has a larger hydrated ionic radii, it was found to have removed more efficiently than either Hg(II) or Cd(II) indicating the fact that Co(II) might have been coordinated to the various coordinating sites other than the –COOH groups of the adsorbent. The presence of lateral interactions in the case of Co(II) adsorption was illustrated by the low $\Delta q\%$ values with respect to the Freundlich isotherm.

The van't Hoff plots, ln $b' \text{ versus } 1/T$, were used to calculate the values of $\Delta H^0$ and were found to be 29.17, 27.81, 32.13 and 7.15 kJ/mol, for Pb(II), Co(II), Hg(II) and Cd(II) respectively suggesting the endothermic nature of adsorption. The negative values of $\Delta G^0$ indicated the feasibility and the spontaneous nature of
sorption. The relatively small positive values of $\Delta S^\theta$ found to be 163.84, 144.16, 167.91 and 92.20 J/mol/K respectively for Pb(II), Co(II), Hg(II) and Cd(II) suggested the increase in randomness at the solid–solution interface during adsorption and indicated no significant structural change occurred as a result of adsorption in the adsorbent material. The feasibility was further tested by computing the equilibrium parameter $R_L$. The isosteric heats of adsorption were found to be independent of adsorption densities advocating the homogeneity of the surface sites.

The present work thus was successful as a scientific challenge in revealing the basis of the metal sorption phenomenon. But the efficacy of PGBS-COOH was further proved by comparing its adsorption capacity with other reported adsorbents and also with the adsorption characteristics of Ceralite IRC-50. Ion exchange resins are considered as a commodity on the market with high cost. Even if a small share of the volume sales of ion-exchanger is replaced by cheaper adsorbents like PGBS-COOH, it would be appropriate and advantageous to small communities, especially in developing countries because of the high metal removal efficiency, simplicity, and ease of construction, operation and maintenance.

Practical viability of the newly developed adsorbent was further validated by treating it with real/simulated/synthetic wastewaters containing different metal ions studied. The effect of adsorbent dose on metal ion removal by PGBS-COOH was examined. The percentage adsorption increased with increasing adsorbent dose, however, unit adsorption or adsorption per unit mass of adsorbent decreased, the effect being more pronounced when the adsorbent dose was higher. The results of the experiment were used to develop mathematical relationships to predict theoretically the percentage removal of each metal ion with a specified adsorbent dose.
To highlight the economic aspect of the adsorbent, regeneration and reusability studies in several cycles were successfully carried out. Studies pertaining to adsorbent regeneration and metal readsoption were carried out in three consecutive cycles. PGBS-COOH undergoing successive adsorption–desorption processes retained good metal adsorption capacity even after three cycles. But the efficiency decreased during the II and III cycles due to incomplete desorption of the bound ions from the adsorbent. Even though different reagents had been tested, the ability of HCl at 0.2 M concentration to remove most of the adsorbed metal ions may be attributed to ion exchange.

The concept of the operational line helps in evaluating the theoretical number of stages for the removal of metal ions with a specified initial concentration. When the initial metal ion concentration was taken as 300 mg/L each for Pb(II), Co(II), Hg(II) and 150 mg/L for Cd(II), the residual Pb(II), Co(II), Hg(II) and Cd(II) concentration leaving the second stages were graphically found to be 15.2, 39.4, 58.5 and 15.0 mg/L respectively. The present study thus opened up wide scope for further investigation so that the environmentalists could restrict heavy metal pollution and improve the quality of water in an effective manner. It can easily be envisaged that these types of cheaper sorbents would open up new, particularly environmental, markets so far non-accessible to ion exchange resins because of their excessive costs which make them unaffordable for clean-up operation applications.

Water pollution by chromium is of considerable concern, as this metal has found widespread use in electroplating, leather tanning, metal finishing, nuclear power plant, textile industries, and chromate preparation. The hexavalent form is highly toxic than the trivalent and the maximum levels permitted in wastewater is 0.05 mg/L and the metal-finishing industries are facing nowadays the difficulty of disposal of wastewater laden with Cr(VI). In the present study two low-cost
sorbents, i.e., polymer grafted banana stalk with-NH$_3^+$Cl$^-$ functional group (PGBS-NH$_3^+$Cl$^-$) and formaldehyde treated banana stalk with hydrous ferric oxide encapsulated in it (FBS-HFO) were successfully employed for Cr(VI) removal. The present work demonstrated that a commercial anion exchanger Duolite A-7 also have a large collective adsorption with Cr(VI) ion from aqueous solution.

From the TG-DTG curves of the samples the initial decomposition temperature, $T_{Di}$ of PGBS-NH$_3^+$Cl$^-$ and FBS-HFO were found to be 205 and 210 °C respectively which were higher than original BS illustrating the increased thermal stability of the modified materials over BS. The $E_a$ values were calculated by the Horowitz and Metzger method. It was found that $E_a$ values for the I stage thermal composition of PGBS-NH$_3^+$Cl$^-$ and FBS-HFO were 96.0 and 90.7 kJ/mol respectively which were higher than that of BS indicating the stability of the modified materials.

SEM analyses revealed that the size of the voids in the original BS was reduced after graft polymerization to form PGBS-NH$_3^+$Cl$^-$ with a rough surface caused by the rigid and hydrophobic nature of the NN'-methylenebisacrylamide-crosslinks. The porous nature provides new adsorption sites from interior cavities to participate in binding of metal ions. The SEM image of FBS-HFO indicated the presence of folds on the surface, which resulted during the polymerization process with formaldehyde. Cracks and irregularities which are beneficial for the metal adsorption were clearly visible in the SEM image of FBS-HFO.

Detailed batch studies with the selected adsorbents, had been carried out in the present investigation. The effects of pH, contact time, adsorbent concentration and temperature on metal adsorption were investigated using batch experiments. The optimum pH range for maximum removal of Cr(VI) by PGBS-NH$_3^+$Cl$^-$ was found to be 3.5–6.0 and at this pH range the removal was found to be 99.9 and 95.5 % from an initial Cr(VI) concentration of 50 and 100 mg/L respectively. The decrease
Summary

in removal of Cr(VI) at very low pH is that the protonated amine groups would be saturated by counter anions present in the solution. Since the pH_{pzc} of PGBS-NH₃⁺Cl⁻ is 6.7, the surface charge of the adsorbent is negative above 6.7 and therefore hinders the adsorption of Cr(VI) oxy-anions at the higher pH range. The reduction in sorption at alkaline pH may also be attributed to the abundance of OH⁻ ions which compete with HCrO₄⁻ or CrO₄²⁻. Cr(VI) interaction with PGBS-NH₃⁺Cl⁻ is considered as the exchange with Cl⁻ ions and the possible mechanism was suggested. Conclusive evidence regarding the nature of Cr(VI) bondage was drawn from IR spectral data.

A maximum removal of 99.7 and 92.4 % Cr(VI) was observed for FBS-HFO in the pH range of 2.5–3.5 at an initial Cr(VI) concentration of 25.0 and 50.0 mg/L respectively. The decrease in Cr(VI) extraction at pH < 2.5 was due to the formation of a non anionic species, H₂CrO₄ which did not take part in the anion exchange process. The Cr(VI) adsorption by FBS-HFO can be explained by a mechanism whereby HCrO₄⁻ undergoes ligand exchange reaction with FBS-HFO coordinated water. The decrease in the removal efficiency at higher pH may be due to the protolysis of hydrated water on the adsorbent bound iron. The higher concentration of OH⁻ ions present in the reaction mixture at higher pH competes with Cr(VI) species (CrO₄²⁻) for the adsorption sites.

Maximum removal of Cr(VI) by Duolite A-7 occurred at pH range of 2.0–3.0. The extent of Cr(VI) adsorption at an initial concentration of 25 and 50 mg/L decreased from 99.9 to 21.2 % and from 93.2 to 19.1 % respectively when the pH of the system was varied from 3.0 to 8.0. The Cr(VI) removal by BS was found to be very much lesser than with the other adsorbents under study. The negative charge associated with BS when in contact with water restricts the approach of Cr(VI) anions towards the BS.
The influence of adsorbent dosage on percentage adsorption and equilibrium uptake indicated that as the dosage increased the percentage adsorption of Cr(VI) also increased for all the three sorbents under study. This is due to the availability of more and more binding sites for linkage of Cr(VI) species. After a particular dose of sorbent, further increase in adsorbent dosage did not cause significant improvement in adsorption. This seems to be due to the binding of almost all ions to the sorbent and the establishment of equilibrium between the ions bound to the sorbent and those remaining unadsorbed in the solution. As a result, the removal of a given amount of Cr(VI) can be accomplished with greater economy of adsorbent if the solution is treated with separate small batches of adsorbent rather than in a single batch, with filtration between each stage.

To predict the efficiency and feasibility of the sorbents, the time taken to attain equilibrium was understood. Equilibrium was reached at 1.5 h contact time when PGBS-NH$_3^+$Cl$^-+Cr$ was agitated with different concentrations of Cr(VI). By decreasing the concentration of the Cr(VI) solution from 250 to 100 mg/L, the percentage removal increased from 65.1 to 96.9%, whereas the removal efficiency decreased from 81.4 to 48.5 mg/g at a pH of 2.5 and 30 °C. Different initial Cr(VI) concentrations, viz., 25, 50, 75 and 100 mg/L were treated with FBS-HFO and the equilibrium time was found to be independent of initial adsorbate concentration. The percentage removal of Cr(VI) from these initial concentrations was found to be 99.8, 93.4, 89.5 and 85.2 %, respectively. When Cr(VI) solutions of 25, 50, 75 and 100 mol/L concentration were treated by Duolite A-7, at pH 3.0 the removal of Cr(VI) in the initial period was very rapid as all the reaction sites were vacant. The transitional phase which followed had a slow rate of uptake almost reaching a constant value within 4 h. The data showed that as the initial concentration of Cr(VI) increased from 25 to 100 mg/L the percentage adsorption decreased from 99.6 to 85.8 % at this equilibrium time.
The mechanism involved in the adsorption process of Cr(VI) by PGBS-NH$_3^+$Cl$^-$ was understood by testing the observed $q_t$ values at various time intervals in different diffusion plots. Intraparticle diffusion plots, which link the solid phase concentration and the square root of time had initial steep-sloped portions followed by only a small linear portion corresponding to the intraparticle diffusion and then ended with a plateau representing the equilibrium. The initial steep-sloped portion is attributed to external surface adsorption or instantaneous adsorption, and the subsequent curved portion related to the boundary layer diffusion while the gentle-sloped portion is attributed to gradual adsorption.

The values of diffusion coefficients $D_1$ and $D_2$ were calculated from the slopes at initial period of the plots of the $\frac{q_t}{q_e}$ against $t^{1/2}$ and from the linear plots of $\ln\left[1-\frac{q_t}{q_e}\right]$ versus $t$. The $D_1$ values were found to be $1.26 \times 10^{-8}$, $1.14 \times 10^{-8}$, $1.11 \times 10^{-8}$ and $1.03 \times 10^{-8}$ cm$^2$/s respectively for an initial Cr(VI) concentrations of 100, 150, 200 and 250 mg/L. While the $D_1$ values decreased and $D_2$ values increased with increase of initial concentration of Cr(VI). The $D_2$ values obtained were $6.88 \times 10^{-9}$, $7.71 \times 10^{-9}$, $8.84 \times 10^{-9}$ and $9.50 \times 10^{-9}$ cm$^2$/s respectively for initial Cr(VI) concentrations of 100, 150, 200 and 250 mg/L. The kinetic data were further analyzed using the mathematical equations suggested by Boyd et al. and Reichenberg for identifying whether the ongoing process is particle diffusion or film diffusion. At low concentrations, $Bt$ versus $t$ plots did not pass through the origin suggesting that the rate-controlling parameter was film diffusion. But, at higher concentrations, the $Bt$ versus $t$ plots moved towards the origin, indicating that particle diffusion was also involved as the rate-controlling parameter. The effective diffusion coefficients for different initial concentrations, found from the slope of the $Bt$ versus $t$ plots, were calculated and reported. The film diffusion
coefficient, $D_f$, and pore diffusion coefficient, $D_p$, were calculated and it was found that the $D_f$ values were within the range of $10^{-6}$–$10^{-8}$ cm$^2$/s indicating that film diffusion to be rate limiting step.

Good linearization of the experimental data was observed for the $\ln \left( \frac{C_t}{C_o} - \frac{1}{1 + m K_L} \right)$ versus $t$ plots, thereby implying that the Cr(VI) uptake rate by BS-HFO is governed by mass transfer through a liquid film boundary. The values of the surface mass-transfer coefficient, $K_L$, for the adsorption of Cr(VI) onto FBS-HFO were found to be $3.64 \times 10^{-6}$, $1.89 \times 10^{-6}$, $1.71 \times 10^{-6}$ and $1.17 \times 10^{-6}$ cm/s for initial Cr(VI) concentrations of 25, 50, 75 and 100 mg/L respectively.

The adsorption behaviour of Duolite A-7 for the removal of Cr(VI) was studied by the kinetic profiles of solutions whose concentrations varied from 25 to 100 mg/L. The sorption of Cr(VI) from liquid phase to solid phase was considered as a simple diffusion controlled first-order reversible kinetic model validated by the straight line plots of $\ln \left[ 1 - \frac{q_t}{q_e} \right]$ versus $t$ at different concentrations. For an initial concentration of 25, 50, 75 and 100 mg/L of Cr(VI), the values of overall rate constants $k'$ were found to be 2.86, 2.36, 1.82 and 1.42 s$^{-1}$ respectively. It was observed that the forward rate constants for the removal of chromium were much higher than the backward rate constants namely the desorption process.

Isotherm study was carried out at 20, 30, 40 and 50°C with a view to elucidate the binding mechanisms and the relative affinity of Cr(VI) for the materials under study, and to compare the adsorption capacities of the adsorbents. The steepness of the isotherms decreased in the order, PGBS-NH$_3^+$Cl$^-$ > Duolite A-7 > FBS-HFO and thereby exhibited decreasing trend of sorbate affinity to Cr(VI). Langmuir, Freundlich and Redlich–Peterson isotherms models were examined and in each case the isotherm parameters were determined. The validity of each model was
Summary
tested by the normalized standard deviation method and also the best fit and the values of $r^2$ corresponding the linear forms of the isotherm equations. It was concluded that the adsorption of Cr(VI) on the three sorbents followed the Redlich–Peterson isotherm models well and the Freundlich model as the least. The high magnitude of Freundlich constant $K_F$ and $n$ for PGBS-NH$_3^+\text{Cl}^-$ reiterated its superiority further. The values of adsorption capacity $Q^o$ were 101.96 mg/g for PGBS-NH$_3^+\text{Cl}^-$, 83.90 mg/g for FBS-HFO and 97.34 mg/g for Duolite, at 30 °C. The monolayer sorptive capacities were used to estimate the specific surface area, $S_s$ of the adsorbents at different temperatures.

The thermodynamic values of $\Delta G^o$, $\Delta H^o$ and $\Delta S^o$ for Cr(VI) adsorption by the three adsorbents were calculated. The values of $\Delta H^o$ were negative suggesting the exothermic nature of the sorption process. The negative values of $\Delta S^o$, -21.12, -70.47 and -66.93 J/mol/K for Cr(VI) adsorption onto PGBS-NH$_3^+\text{Cl}^-$, FBS-HFO and Duolite A-7 respectively showed the decreased randomness at the solid–solution interface during the adsorption process and also reflected the affinity of the adsorbent material for the metal ions. The efficiency of the sorbents was tested with a simulated wastewater based on a chrome plating unit wastewater. All the three sorbents were successful in removing practically all Cr(VI), inspite of the foreign anions present. The amount of PGBS-NH$_3^+\text{Cl}^-$, FBS-HFO and Duolite A-7 needed for complete removal of 25 mg/L of Cr(VI) present in the wastewater sample were 3.0, 7.8 and 6.5 g/L respectively, highlighting the superiority of PGBS-NH$_3^+\text{Cl}^-$. Regeneration studies demonstrated that the sorbents can be recovered effectively for the re-adsorption of the Cr(VI) ions using 0.25 N NaOH. Studies to this effect illustrated that the sorbents undergoing successive adsorption–desorption processes retained fairly good metal adsorption capacity even after three cycles. The time needed for the efficient release of bound Cr(VI) ions was monitored as 3
h, for PGBS-NH$_3^+$Cl$^-$ and 5 h for FBS-HFO and Duolite. Attempts to desorb Cr(VI) from Cr(VI) loaded sorbents using distilled water appeared to be futile indicating lack of physical forces operating in the sorption process.

Empirical design procedures based on sorption equilibrium studies were used to predict the adsorber size and performance. A batch design was formulated for the 90% removal of Cr(VI) solution of 100 mg/L concentration at 30°C for predicting the mass of PGBS-NH$_3^+$Cl$^-$, FBS-HFO and Duolite A-7 required for the change in solution concentration at different solution volumes. The amounts of adsorbent required were 2.28, 4.56, 11.41 and 20.52 g PGBS-NH$_3^+$Cl$^-$, 3.01, 6.02, 15.05 and 27.09 g FBS-HFO and 3.03, 6.06, 15.15 and 27.28 g for Duolite A-7 for Cr(VI) solution volume of 1, 2, 5 and 9 L, respectively. Even though the adsorption capacity of FBS-HFO was found to be slightly lower than Duolite A-7, it was found that slightly lesser amount of FBS-HFO was needed for the 90% removal compared with Duolite A-7 in all cases. These anion exchangers are thus attractive sorbents for the treatment of wastewater containing Cr(VI) ion at trace levels prove to be a very viable and alternative to other traditional treatment processes.

Considerable documentation regarding the health threat of arsenic contamination in groundwater and drinking water is now available. Daily consumption of water with greater than 0.01 mg/L of arsenic, less than 0.2% of the fatal dose, can lead to problems affecting the skin and the circulatory and nervous systems and developing cancer of the bladder, liver, and kidney. Therefore the arsenic problem is of primary concern in many countries and research into the development of cost-competitive technologies for arsenic removal from water sources to meet the MCL value is urgent. The present study investigated a possible strategy for the removal of arsenic by employing iron(III) loaded macroporous resin as adsorbent by utilizing both the ion exchange nature of the cation exchanger Duolite C26 and the high affinity of Fe towards inorganic arsenic. This work
Summary

further focussed on investigating how various experimental parameters, like pH, adsorbent dose, contact time, temperature and the concentration of As species influence arsenic (both As(V) and As(III)) adsorption.

Studying the distribution ratio of ferric ion between the Duolite and aqueous phases under various pH conditions revealed that maximum loading of Fe occurred at a pH of 2.0–2.5 which would prevent hydrolysis of ferric ions also. This is due to Fe\(^{3+}\) exchange with the H\(^+\) ions of sulphonic acid groups of the resin. Loading of the resin with Fe was performed in batch conditions by shaking 100 mg Duolite with 50 mL of iron(III) solutions of varying concentrations ranging from 50 to 600 mg/L for 3 h at room temperature and at a pH of 2.0. The maximum loading capacity for ferric ions at pH 2.0 was found to be 56.10 mg/g from the adsorption isotherm. It was then converted to hydrous ferric oxide loaded resin (HFOLR) by treating with a mixture of NaOH and NaCl solutions.

A detailed study of nitrogen adsorption–desorption isotherm of HFOLR revealed many key aspects regarding the pore distribution characteristics. HFOLR showed a pore size distribution with a pore diameter of 120.62 Å, a small surface area of 1.51 m\(^2\)/g, a total pore volume of 2.27 \times 10^{-3} \text{ mL/g} (for pores smaller than diameter of 1622.5 Å) and micropore volume of 4.44 \times 10^{-4} \text{ mL/g}. The observed micropore area (1.106 m\(^2\)/g) was much higher than the external surface area (4.04 \times 10^{-1} \text{ m}^2/\text{g}).

The pH\(_{pzc}\) of HFOLR was found to be 8.4 which is consistent with earlier values reported for HFO systems. For an initial concentration of 10 mg/L, a maximum adsorption of 99.6 % of As(V) on HFOLR occurred in the pH range of 3.0–4.0. When the initial concentration was 25 mg/L, a maximum removal of 86.6 % occurred. At very low pH value, As(V) predominantly exists as a neutral species, $\text{H}_3\text{AsO}_4$ which is difficult to attach to exchange sites of the sorbent for anion exchange. Arsenite was found to be removed from the aqueous media less
efficiently than arsenate and the maximum removal occurred at a pH of 7.0, where 90.8 and 75.5 % removal was possible from an initial As(III) concentration of 10 and 25 mg/L respectively.

The effect of ionic strength on As(V) and As(III) adsorption onto HFOLR provided a measure of the relative bonding affinity of these ions for surface hydroxyl groups. It was noted that the arsenate adsorption on HFOLR showed no dependence on ionic strength. A slight increase in adsorption of As(III) occurred with increase in ionic strength inferring an innersphere complex. Surface complex theory was successfully applied to explain the nature of interaction of As species with the surface functional groups of HFOLR. Positive identification of adsorbed arsenate/arsenite species was provided using the FTIR and XRD techniques too. The surface morphology and microstructure of the samples were analysed by the SEM observation. Energy dispersive analysis of X-ray (EDAX) was used for characterizing the elements associated with the adsorbent before and after adsorption and prominent signals corresponding to As are observed for As(III) and As(V) laden HFOLR.

The XRD patterns for the adsorbent did not yield any crystalline peaks suggesting the amorphous nature due to the fact that the crystallization of iron oxides is strongly retarded by the presence of the anionic resin particles. The XRD analysis also confirmed that the pure iron(III) oxide prepared in this study was amorphous, presumably due to a short aging time. After arsenic(V) sorption, the loaded sorbent yielded the characteristic bands corresponding to crystalline ferric arsenate or ferric arsenite suggesting the formation of specific chemical substances after adsorption.

It took 8 h to attain the adsorption equilibrium for arsenic(V) and 5 h for arsenic(III) for four different concentrations indicating specific adsorption. Good fits were not observed the sorption with time requires using the traditional pseudo-
first-order and pseudo-second-order kinetic models. Intraparticle diffusion model was used for understanding the sorption mechanism. Multilinear plots indicating more than two steps in the sorption phenomenon were obtained. An initial small sharper portion corresponded to the external surface adsorption or instantaneous adsorption stage and is followed by a portion representing gradual adsorption stage, where intraparticle diffusion controls the rate. The third portion is the final equilibrium stage where intraparticle diffusion starts to slow down due to extremely low adsorbate concentrations in the solution. The diffusion rate for As(V) was found to be two times faster than that of As(III), indicating that arsenate ion is more easily diffused and transported into HFOLR pores than arsenite. Arsenite ion has a plane-triangular shape, while arsenate ion has a tetrahedral shape and the radii of HAsO₄²⁻, H₂AsO₄⁻ and H₃AsO₄ are 3.97, 4.16 and 4.16 Å respectively and for H₂AsO₃⁻ and H₃AsO₃ are 4.80 Å each. Thus arsenate ions are able to diffuse onto the pore channel of HFOLR more easily than arsenite ions and hence take longer period for attaining equilibrium. The intraparticle diffusion rate constant, \( k_p \) were found to be 0.0191, 0.0563, 0.0788 and 0.1225 mg/g s\(^{1/2}\) for As(V) and 0.0186, 0.0517, 0.0760 and 0.0942 mg/g s\(^{1/2}\) for As(III) for initial concentrations of 10, 25, 50 and 100 mg/L respectively.

To establish the most proper relationship for the equilibrium curves, isotherm studies were performed for both As(V) and As(III) ions using four different isotherm equations namely, Langmuir, Freundlich, Temkin and Dubinin–Radushkevich. The Langmuir and Temkin equations agreed very well with the equilibrium isotherm for As(V) as well as As(III) for the entire concentration range studied. However, to fit the isotherm data by the Freundlich and Dubinin–Radushkevich equations gave low correlation and higher \( \Delta q(%) \). The maximal adsorption capacities of As(V) and As(III) were 36.2 and 25.8 mg/g at 30 °C, comparatively higher than that of other adsorbents reported in the literature.
The adsorption capacities also increased with the increase of temperature. The values of Gibbs free energy of adsorption for As(V) was found to be -22.6, -23.7, -25.0 and -26.6 kJ/mol; the corresponding values for As(III) were -21.8, -23.1, -24.4 and -26.0 kJ/mol respectively at 30, 40, 50 and 60 °C. These values revealed that the feasibility of the adsorption process increased with increase in temperature. The value of the equilibrium binding constant (A) calculated using Temkin equation was found to be larger for As(V)–HFOLR system than that for As(III)–HFOLR interaction. This indicated that the adsorbate–adsorbate interaction is larger for the former than that of the latter. With increase in temperature the values of A showed increasing trend suggesting stronger interaction of the As species at elevated temperatures.

The simulated water samples based on groundwater of New Jersey, USA, which contained arsenic together with cations based on, Al, Mg, Fe, Ca and Mn as well as anions like, fluoride, chloride, sulfate and carbonate, were treated by HFOLR to demonstrate its efficiency in removing As(III) and As(V) ions. Arsenic content could be brought down from 1.0 mg/L to well below 0.01 mg/L, the maximum permissible level as per WHO norms, with an HFOLR dose of 2.5 g/L for As(V) and 3.0 g/L for As(III). The possibility of regeneration and reuse of the adsorbent for determining the ability of the arsenic to be stripped selectively from the functionalized sorbent, using several eluents, such as hydrochloric acid, citric acid and sodium hydroxide was explored. More than 97 % of the arsenic adsorbed to the HFOLR was desorbed by 0.1 M NaOH in less than 10 h suggested the recyclability of the adsorbent. The present system is appropriate and advantageous to small communities, especially in developing countries because of the high arsenic removal efficiency, simplicity, and eases of construction, operation and maintenance and promises to be a competitive choice amongst the treatment systems available for arsenic removal.
In conclusion, our results suggest that PGBS-COOH, PGBS-NH$_3^+$Cl$^-$, FBS-HFO and HFOLR can be good heavy metal adsorbers and have great potential applications in environmental protection. The feasibility of using lignocellulosic-based cation exchanger (PGBS-COOH) for the removal of heavy metals, such as Pb(II), Hg(II), Co(II) and Cd(II) is postulated only through batch operations; however, further work in column evaluation need to be done. The above conclusion is valid for the adsorption of individual metal ions. The results may differ when two or more metal ions are simultaneously present (and competing with the adsorption sites) in solutions. Although real industrial wastewaters contain a mix of more than one metal, it is essential initially to consider single metal systems to reduce the complexity of using real industrial effluent. Having said this, an important area for further study is determining the adsorption parameters of multicomponent systems as well as real industry effluents. The multicomponent equilibrium isotherms and kinetic profiles should be considered to better understand the interaction of heavy metals in the solutions and with the adsorbent systems.

The obtained results from the batch studies indicate that lignocellulosic-based anion exchangers (PGBS-NH$_3^+$Cl$^-$ and FBS-HFO) could be effectively used to remove Cr(VI) from aqueous solutions. Further work should be carried out to better characterize the adsorption behaviour of these adsorbents, by studying other pollutants (As(III), As(V), V(IV), PO$_4^{3-}$/HPO$_4^{2-}$/H$_2$PO$_4^-$) adsorption from solutions both separately and under competition and taking into account parameters, such as the adsorbate pH, atomic/molecular size, charge and possible interactions to a surface level.

The results of the present study also demonstrate the usefulness of the examined HFOLR in improving As(III) and As(V) immobilization. Further experiments are in progress in order to validate the efficiency of this material in the
cleanup of real industry effluents and contaminated groundwater. Column flow-through tests, of this newly developed adsorbent in globular form, should be conducted before any practical application. The results from batch and column operations may be of value in developing sound remediation strategies for water contaminated with As(III) and As(V) ions.

Cost analysis for the preparation of the above mentioned lignocellulosic-based adsorbents was not carried out in detail. Since banana stalk, the precursor material is abundant in India, the cost of these adsorbents is expected to be economical. However, a detailed cost analysis should be performed for each of the adsorbents examined. As an extension of this research programme, we are working on developing new adsorbents from banana stalk through graft copolymerization of other vinyl monomers (acrylonitrile and acrylic acid) using different redox systems and further investigations on their applications to water treatment are in progress.