SUMMARY

Industrial activities are major sources of water pollution, particularly where the toxic metals are concerned. The pollution of water resources due to the indiscriminate disposal of heavy metals which are introduced into water streams from various industries has been causing worldwide concern for the last few decades. Once discharged into waste stream, these metals get accumulated through food chain, thus becoming a serious threat to the environment. These metals are non-biodegradable and have great environmental, public and economic impact. The removal of heavy metals in an effective manner from water and wastewater is, thus, ecologically very important.

A survey of literature was carried out to get an insight into the various methods used for treatment of wastewater. Different treatment techniques for wastewater laden with heavy metals have been developed in recent years both to decrease the amount of wastewater produced and to improve the quality of the treated effluent. Most of these methods involve high capital cost with recurring expenses which cannot be afforded by small and medium scale industries. Studies on treatment of wastewater bearing heavy metals have revealed adsorption to be a highly effective, cheap and easy method among these physico-chemical treatment processes. Adsorption on activated carbon and activated carbon obtained from agricultural waste material are widely used. However, the use of agricultural waste material as adsorbent reduces the cost to further extent providing an almost equal efficiency. Research in the field of metal removal based upon using agricultural waste material (untreated and treated) as adsorbent has gained a lot of importance in the recent years. In the present study, the use of locally available saw dust from *Tectona grandis* and rice husk has been undertaken with a view to obtain a cost effective adsorbent for removal of metal ions. Both batch as well as column studies have been undertaken. For carrying out column studies two types of columns have been used namely sequential bed column and vertical column. The study is focused on the removal of Pb(II), Zn(II) and Mn(II) on rice husk, thiolated rice husk, esterified rice husk, saw dust, thiolated saw dust and esterified saw dust when present individually and to study the effect of presence of Ni(II), Cu(II) and Fe(II) on the adsorption of Pb(II), Zn(II) and Mn(II) respectively.

The rice (*Oryza sativa*) husk (variety PR 106) was procured from the agricultural land of Sangrur and saw dust of *Tectona Grandis* was procured from saw mill of Sangrur, Punjab, India. The rice husk/saw dust were washed repeatedly with distilled water and
dried at a temperature of 80°C for 4 hours. The samples thus obtained were subjected to sieve analysis and particles of desired size were collected and used for adsorption studies. Chemical modification of rice husk/saw dust has been carried out by treatment with thioglycollic acid to get thiolated rice husk/saw dust. Similarly esterified rice husk/saw dust was obtained by treatment of rice husk/saw dust with succinic anhydride in the presence of triethyl amine. Characterization of the adsorbent has been done by carrying out a proximate analysis of rice husk and saw dust, determination of degree of thiolation/esterification and infra red spectral studies. The infrared spectra for all the adsorbents under study show bands between 3420-3300 cm\(^{-1}\) due to the surface hydroxyl groups, chemisorbed water and between 2950-2900 cm\(^{-1}\), attributed to symmetric or asymmetric C–H and the symmetric stretching vibration of CH\(_2\). The peaks observed between 1720-1651 cm\(^{-1}\) are indicative of stretching vibration of C–O bonds due to non-ionic carboxyl groups (–COOH, –COOCH\(_3\)) and the peaks observed between 1020 to 1158 cm\(^{-1}\) are indicative of aliphatic ethers as well as of SO\(_3\) stretching modes. For thiolated rice husk/saw dust bands present below 800 cm\(^{-1}\) can be assigned to sulphur functional (–SH) groups and in case of esterified rice husk/saw dust, the peaks observed around 1425-1500 cm\(^{-1}\) are indicative of moderate C–O–H bending of ester.

The degree of thiolation/esterification of thiolated/esterified material has been studied by reported methods. Further the surface area of rice husk/saw dust was estimated by iodine method. The surface area for rice husk and saw dust was found to be 200.9 and 179.7 m\(^2\)/g respectively.

Batch adsorption studies have been carried out to optimize the conditions for maximum adsorption of Pb(II), Zn(II) and Mn(II) onto the adsorbents under study namely rice husk, thiolated rice husk, esterified rice husk, saw dust, thiolated saw dust and esterified saw dust. Studies have been carried out to see the effect of solution pH, concentration, contact time, temperature as well as particle size of adsorbent. The pH has been varied in the range 2–8 for the metal ions Pb(II), Mn(II) and 4–9 for Zn(II) ions. The contact time has been varied from 30 to 210 minutes for all the adsorbents/metals under study. Metal ion concentration was varied between 30–300 mg/l, particle size of adsorbents studied was varied from 212, 425 and 600 micron and the temperature of adsorption was studied at 298, 308 and 318K.
Results show that maximum removal of Pb(II) ions occurs at pH 5 for all the adsorbents studied for a contact time of 180 minutes for rice husk and saw dust and 150 minutes for chemically modified forms. The increase in amount of metal ion adsorbed with pH is explained on the basis that at low pH, there is competition of the H⁺ ions with metal ions, for occupancy of the adsorption sites. At higher pH there is formation of precipitate due to the formation of hydroxyl species. The study of effect of contact time shows that the amount adsorbed is greater in the initial stages of adsorption upto 60 minutes, thereafter the increase in amount adsorbed with increase in contact time is slower probably due to the fact that the number of vacant adsorption sites are greater in the initial stages. From the study involving change in metal ion concentration it was found that amount of Pb(II) ions adsorbed increases with increase of concentration from 30 to 300 mg/l for all the adsorbents under study. However, percentage removal increases with decrease in the concentration. The increase in percentage removal with dilution is probably due to availability of larger number of surface sites of the adsorbent for a relatively small number of adsorbing species at high dilution.

The effect of particle size has been studied on 212, 425 and 600 micron for the adsorption of Pb(II) ions on all the adsorbents under study. It is found that the amount of metal ions adsorbed increases with decrease in particle size of the adsorbent. Smaller particle size will lead to increase in surface area and thus increase in the adsorption opportunity at the outer surface of the adsorbent. Hence, 212 micron particle size is used in equilibrium studies for all the adsorbents under study.

Similarly studies for zinc ions show that the amount of Zn(II) adsorbed increases with increase in pH. The amount adsorbed increases upto pH 8, further increase in pH shows a decline. The optimum pH for the adsorption for zinc is thus 8. The sorption is lower in acidic ranges because, due to high positive charge density there is electrostatic repulsion between the positively charged adsorbent and zinc ions resulting in lesser adsorption (Bhattacharya et al., 2006). With increasing pH, electrostatic repulsions decrease due to reduction of positive charge density on the sorption sites of adsorbent thus resulting in an increase in adsorption, on increasing the pH to 9 soluble hydroxyl complexes of the type [Zn(OH)₄]²⁻ are formed. The amount of Zn(II) ions adsorbed increases with increase of concentration from 30-300 mg/L, however, percentage removal increases with decrease in the concentration for all the adsorbents under study. The increase in percentage removal with dilution is probably due to availability of
larger number of surface sites of the adsorbent for a relatively small number of adsorbing species at high dilution

The amount of Zn(II) ions adsorbed increases with increase in contact time, the equilibrium being observed at 180 minutes for saw dust and 150 minutes for rice husk, thiolated rice husk, esterified rice husk, thiolated saw dust and esterified saw dust. The variation in particle size from 212, 425 and 600 micron shows that the amount of Zn(II) ions adsorbed increases with decrease in particle size of the adsorbent. Smaller particle size will lead to increase in surface area and thus increase in the adsorption opportunity at the outer surface of the adsorbent. Hence, 212 micron particle size is used in equilibrium studies for all the adsorbents used.

The pH has been varied in the range 2–8 for the adsorption of Mn(II) ions on rice husk, thiolated rice husk, esterified rice husk, saw dust, thiolated saw dust and esterified saw dust respectively. It is found that the amount of Mn(II) adsorbed increases as the pH is increased from 2 to 5 where a maxima is obtained, further increase in pH shows a decline. Studies thus suggest that the governing factor affecting the adsorption for all adsorbents is the competition of the H\(^+\) ions with metal ions at low pH values for occupancy of the adsorption sites, at higher pH precipitation of hydroxyl species occurs.

The variation in the initial concentration from 30-300 mg/L for the adsorption of Mn(II) ions shows that the amount of Mn(II) ions adsorbed increases with increase of concentration from 30-300 mg/L, however percentage removal increases with decrease in the concentration for all the adsorbents under study which as explained earlier is due to the availability of a larger number of surface sites of the adsorbent for a relatively small number of adsorbing species at high dilution.

The effect of contact time has been studied in the range 30-180 minutes for the adsorption of Mn(II) ions on all the adsorbents under study. The amount of metal ions adsorbed increases with increase in contact time until the attainment of equilibrium. For adsorption of Mn(II) the equilibrium is observed at 180 minutes for rice husk, saw dust, thiolated rice husk, thiolated saw dust and 150 minutes for esterified rice husk and esterified saw dust respectively. As contact time was increased, more and more functional groups participated in adsorption of the metal ions until it reached equilibrium.
The effect of particle size has been studied on 212, 425 and 600 micron for the adsorption of Mn(II) ions on all the adsorbents under study and amount of metal ions adsorbed increases with decrease in particle size of the adsorbent. Smaller particle size will lead to increase in surface area and thus increase in the adsorption opportunity at the outer surface of the adsorbent. Hence, 212 micron particle size is used in equilibrium studies for all the adsorbents under study.

The equilibrium data obtained at optimized conditions for all the metal ions studied have been subjected to various adsorption isotherm models such as Freundlich, Langmuir, Dubinin-Radushkevich (D-R), Generalized equations and the isotherm constants have been calculated in each case. It is found that the data obtained for the adsorption of metal ions on all the adsorbents under study fits well to both Freundlich and Langmuir isotherm models indicating favourable and monolayer adsorption. The values of $1<n<10$ indicate the effectiveness of the adsorbent. The values of the dimensionless parameter $R_l$ obtained from the Langmuir plot which gives an idea about the effectiveness of the adsorbent have been calculated. The values of $R_l$ have been found to lie between 0 and 1, for all the cases studied, which suggest favourable adsorption. The data also fits well to the Dubinin-Radushkevich (D-R) model. The value of $E$ obtained from Dubinin-Radushkevich (D-R) isotherm model for Pb(II), Zn (II) and Mn(II) ions for all the adsorbents under study are found between 1 and 16 kJ mol$^{-1}$ thus indicating that physical adsorption is taking place. The equilibrium data for the adsorption of Pb(II), Zn(II) and Mn(II) ions on all the adsorbents fits well to the Generalized isotherm, on the basis of correlation coefficient.

In order to examine the kinetics for adsorption of Pb(II), Zn(II) and Mn(II) ions on all the adsorbents under study, rate equation, Lagergren equation and pseudo second order equation were analysed. Results show that the adsorption of Pb(II) follows pseudo second order kinetics while Zn(II) and Mn(II) follow first order kinetics for all the adsorbents. In order to check the possibility of intraparticle diffusion for adsorption of Pb(II), Zn(II) and Mn(II) ions, the data obtained were fitted to Weber-Morris equation in each. The plots between amount adsorbed and $t^{1/2}$ are straight lines which do not pass through the origin in all the cases studied. This suggests that in addition to surface adsorption, diffusion also occurs, however, diffusion is not the rate determining step. Calculation of the values of $K_p$, the intraparticle diffusion constant, for different adsorbents used in this study show an increase in $K_p$ with decrease in particle size and...
with increase in concentration of metal ions. These indicate that the mechanism of metal ions adsorption by the selected adsorbents is complex and both the surface adsorption and intraparticle diffusion contribute to the rate determining step.

The effect of temperature has been studied at 298, 308 and 318K for the adsorption of Pb(II), Zn(II) and Mn(II) ions on rice husk, thiolated rice husk, esterified rice husk as well as saw dust, thiolated saw dust and esterified saw dust. It is found that the amount of metal ions adsorbed increases with increase in temperature. The results suggest that, the sorption is endothermic in nature. The variation in the extent of adsorption of metal ions on all the adsorbents under study with respect to temperature has been explained based on thermodynamic parameters viz. changes in standard free energy ($\Delta G^0$), enthalpy ($\Delta H^0$) and entropy ($\Delta S^0$) which have been determined from slope and intercept of Van’t Hoff plots. The negative values of change in standard free energies ($\Delta G^0$) indicate feasibility and spontaneous nature of adsorption of metal ions on the adsorbent. The values of $\Delta H^0$ have been found to be positive for all the cases under study which suggest the endothermic nature of adsorption. Similarly, the values of $\Delta S^0$ are positive for all the cases under study. The positive value of $\Delta S^0$ suggests the increase in randomness at solid solution interface during adsorption.

Experiments have been performed to investigate the influence of Ni(II) on uptake of Pb(II), Cu(II) on Zn(II) and Fe(II) on Mn(II) from mixed solutions. It has been found that percentage removal of the metal ions under study namely Pb, Zn and Mn, decreased significantly from binary solutions for all the adsorbents under study. To analyze the effect of the presence of another metal, the Langmuir competitive model was applied to the binary sorption equilibrium data, results show that in all cases, there was an inhibitory effect of one metal on binding of the other metal.

Column experiments have been conducted to understand the adsorption behavior of the metal ions on all the adsorbents under study by sequential bed and vertical columns. The use of the sequential bed adsorption column has been considered since the set-up is simple, no feed pumps or other mechanical devices are required, as the solution is made to flow under gravity, and as such the cost involved for the set-up is low. Besides this, the handling procedure is relatively less cumbersome. The results of the sequential bed adsorption column can be compared with those obtained by using a vertical column.
For column studies solutions of metal ion concentration corresponding to 200, 250 and 300 mg/L have been used and maximum removal was observed for a concentration of 200 mg/L. Removal efficiency decreases with increase in concentration, both for sequential bed as well as vertical columns and this can be explained by the fact that as the concentration of metal ions increases, it causes an increase in the number of ions coming in contact with the adsorbent during the same interval of time, while on the other hand, the number of sites available for adsorption is constant for all concentrations, hence the percentage of metal ions removed is dependent upon initial concentration. In the case of sequential bed column, the adsorption is more that that by the vertical column. In each case, studies have been carried out at flow rates of 1.2, 1.5 and 1.8 l/h. It is observed that removal efficiency decreases with an increase in flow rate for both types of columns. However, the sequential bed column shows a higher value of percentage removal, maximum removal has been obtained at a flow rate of 1.2 l/h in case of both the types of columns. Removal efficiency decreases when the flow rate is increased to 1.5 l/h and further decreases when the flow rate is increased to 1.8 l/h. These observations may be explained on the basis that at higher flow rate due to lesser residence time of solution in bed, the mass transfer is lesser, i.e., lesser adsorption.

Breakthrough curves are very important characteristics for determining the operation and the dynamic response of adsorption column. The breakthrough time depends upon influent metal ion concentrations and flow rate. For present study, the time for 50% breakthrough has been calculated for different flow rates and different influent metal ion concentrations at optimum pH and optimum particle size obtained from batch studies. It has been found that the breakthrough point decreases and breakthrough curve became steeper with increase of influent concentration and with increase of flow rate on all the adsorbent under study. The results also show that the shape of the breakthrough curve is saturated earlier at higher influent concentration and the residence time of the adsorbate in the column would decrease because the front of the adsorption zone quickly reached the top of column. Thomas model and Yoon-Nelsen model has been used to evaluate model parameters and predict the adsorption performance and capacity in sequential bed and vertical column. Prominent and unique characteristic features of the respective models, adsorption capacity (Thomas model) and time for 50% breakthrough (Yoon–Nelson model) have been determined.
Attempt has been made to desorb the metal ions from rice husk, thiolated rice husk, esterified rice husk, saw dust, thiolated saw dust and esterified saw dust using 0.5M solutions of HCl at flow rate 1.2 l/h. Recovery to the extent of 90% has been possible. The higher percentage of desorption indicates that ion exchange mechanism plays a significant role in the sorption process.

The results of this study suggest that rice husk and saw dust are effective adsorbents for Pb(II), Zn(II) and Mn(II) in their original as well as chemically modified (thiolated and esterified) forms and can be effectively used as adsorbents for the removal of metal ions from aqueous solutions. Efficiency of sequential bed adsorption column has been found to be higher than that for a vertical column. Since the experimental set up for a sequential bed adsorption column is extremely simple and involves less capital cost, it can find application in small-scale industries, especially in developing countries.