CHAPTER 5

SUMMARY AND SCOPE FOR FUTURE WORK

5.1 SUMMARY OF WORK DONE

Cashew nut shell is an agricultural waste, generated from the cashew nut processing industries. This material has been found to be a potential adsorbent for the removal of impurities from wastewater. Cashew nut shells were modified by treatment with sulphuric acid. The present investigation shows that cashew nut shell, in its native and modified forms, can be utilized as an effective adsorbent for the treatment of wastewater containing metal ions like Pb(II), Cu(II), Cd(II), Zn(II) and Ni(II). The adsorbents (CNS and STCNS) were characterized by using the FTIR and SEM analyses. The effect of various parameters such as the solution pH, adsorbent dose, contact time, initial metal ion concentration and temperature, on the adsorption of metal ions with CNS and STCNS were studied. Further, based on these studies, the kinetics of adsorption, adsorption isotherms and the thermodynamics of the adsorption process were also explored. In addition, desorption of the metal ions from the loaded adsorbents was also carried out to ascertain the reusability of the adsorbents. The results of the adsorption of metal ions onto the CNS and STCNS are summarized below:

- The FTIR analysis shows that both the CNS and STCNS have a variety of functional groups, such as hydroxyl, carbonyl and carboxyl groups, which may be involved in the potential binding of metal ions onto the adsorbents. The FTIR spectrum
of STCNS as compared to that of CNS, is different, and there is a change in the spectrum observed which confirms the modification. The FTIR spectrum of the STCNS shows that a large proportion of the alcoholic groups of the CNS is converted into ether. This material is also made more carbonaceous. The formation of ethers results in the formulation of a matrix with a highly cross-linked network. The SEM image of the STCNS shows an irregular pattern and a more porous surface than the CNS image. This confirms that the STCNS adsorbent has a more desired surface morphology for metal ion adsorption than the CNS adsorbent.

- The solution pH is one of the most important critical parameters in the adsorption of metal ions from aqueous solutions. The pH value affects the surface charge of the adsorbent, the degree of ionization, and the speciation of adsorbate during the adsorption process. At low pH values, the H\(^+\) ions occupy most of the adsorption sites on the adsorbent surface and only a small amount of metal ions could be adsorbed, because of electrostatic repulsion with H\(^+\) ions on the adsorbent surface. With an increase in the pH value, the adsorbent surface becomes negatively charged, and hence, the adsorption of metal ions increases and reaches the maximum at pH 5.0. The decrease in the adsorption efficiency at higher pH (>5.0) must be due to the formation of metal hydroxide. It can be inferred that a pH of 5.0 is favourable value for metal ion adsorption for both the CNS and STCNS.

- The study of the effect of the adsorbent dosage on the adsorption of metal ions shows that the percentage of metal
ions removed increases with an increase in the adsorbent dosage due to an increase in the surface area. The maximum adsorption of metal ions onto the CNS was found to be 88.98% for Pb(II), 81.02% for Cu(II), 75.35% for Cd(II), 78.15% for Zn(II) and 73.69% for Ni(II) at CNS dose of 3 g/L. For STCNS, the maximum adsorption for Pb(II), Cu(II), Cd(II), Zn(II) and Ni(II) ions was found to be 99.12%, 98.07%, 94.50%, 91.58% and 87.62%, respectively, with an adsorbent dose of 1 g/L.

- Metal ion removal increases with an increase in the contact time and attains the equilibrium at a contact time of 30 min for all the metal ions studied. This is mainly due to the rapid adsorption of metal ions on the external surface of the adsorbent during the initial stages of the process.

- The adsorption kinetics of metal ions onto both the adsorbents were studied by using the pseudo-first order, pseudo-second order and the Elovich kinetic equations. The kinetic results show that the metal ion-adsorbent system cannot be described by the pseudo-first order equation and the Elovich kinetic equation. Since the $R^2$ values obtained for these equations are low, and the calculated $q_e$ values also considerably deviate from the experimental values, the pseudo-second order equation provides the best correlation of the experimental data. It can be inferred from these studies that the chemisorption mechanism is the rate controlling step.

- The adsorption of metal ions onto the CNS and STCNS was found to be controlled by both surface and pore
diffusion, with surface diffusion at the earlier stages followed by pore diffusion at the later stages. It can be confirmed from the Boyd kinetic plot that the external mass transfer is the slowest step involved in the adsorption of metal ions onto the adsorbent. Effective diffusivity values were calculated for the adsorption of metal ions onto the adsorbents.

- The study of the effect of the initial metal ion concentration on metal ions removal shows that there is a decrease in metal ion removal with an increase in its initial metal ion concentrations. But it is also observed that there is an increase in the adsorption capacity with an increase in the metal ion concentration. The decrease in the percentage of metal ion removal can be attributed to the saturation of the available active sites on the adsorbent beyond a certain initial metal ion concentration. The increase in the adsorption capacity may be due to the higher adsorption rate and the utilization of all the available active sites for adsorption at a higher initial metal ion concentration.

- The equilibrium data have been analyzed by using the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich adsorption isotherms. The characteristic parameters for each isotherm and its related $R^2$ values have been determined. The applicability of the Freundlich, Langmuir and Temkin isotherm equations to the metal ions-adsorbent (CNS and STCNS) system indicated that monolayer adsorption and heterogeneous surface conditions exist under the studied experimental conditions. The adsorption of metal ions onto the
adsorbent surface is thus complex, involving more than one mechanism. The values of the equilibrium parameter ($R_L$) from the Langmuir adsorption isotherm, and the ‘$n$’ values from the Freundlich adsorption isotherm indicate, that the adsorption process is favourable for all the metals. The results show that the monolayer adsorption capacity exhibited by the STCNS adsorbent is higher than that of the CNS adsorbent.

- A single-stage batch adsorber was designed for different adsorbent doses to effluent volume ratios for each metal ion-adsorbent system, using the best fitted adsorption isotherm. The batch adsorber design may be useful for an environmental engineer in designing treatment plants for metal ion removal from wastewater.

- The percentage removal of metal ions decreases with an increase in the temperature. This is mainly due to a decrease in surface activity suggesting that the adsorption between the metal ions and the adsorbent is an exothermic process. Thermodynamic parameters such as Gibbs free energy ($\Delta G^\circ$), enthalpy change ($\Delta H^\circ$) and entropy change ($\Delta S^\circ$) were evaluated. The results show that the adsorption of metal ions onto the adsorbents (both CNS and STCNS) is spontaneous and exothermic in nature. The negative value of $\Delta G^\circ$ indicates that the adsorption process is feasible and spontaneous, the negative value of $\Delta H^\circ$ reveals the exothermic nature of adsorption, and $\Delta S^\circ$ can be used to describe the randomness at the adsorbent-solution interface during the adsorption process.
Desorption and regeneration studies show the possibility of regeneration and recovery of the metal ions. Physical adsorption seems to be the main mechanism by which the adsorbates are attached to the adsorbent. It can also be assumed that chemisorption/ion exchange was minimal during the adsorption process. Since about 95% of metal recovery from the spent adsorbent was obtained, it can be inferred that metal ions do not form strong bonds with the adsorbent.

Based on the above observations, it can be concluded that both CNS and STCNS have high potential towards removal of heavy metal ions from an aqueous solution. Comparing CNS and STCNS, the adsorption capacity of STCNS seems to be higher. STCNS is suitable for a wide range of initial metal ion concentrations whereas CNS is applicable only to treat wastewater containing a low metal ion concentration. A small amount of STCNS is sufficient to treat wastewater containing a high concentration of heavy metal ions.

5.2 SCOPE FOR FUTURE WORK

The surface modification of cashew nut shells by sulphuric acid makes them suitable and effective adsorbents for the removal of heavy metal ions from wastewater. The efficiency of the adsorbent can also be improved by optimizing the surface modification procedure. No significant reports regarding the utilization of CNS and STCNS as adsorbents for metal ions removal have ever been reported. CNS also has good potential to treat organic wastes present in water.

Many methods are available to modify the adsorbent surfaces and also many agricultural wastes are available as low-cost adsorbents, which may be utilized and modified by using any of the established surface
modification methods. The prepared adsorbent may definitely be an alternative to commercially available adsorbents.

Furthermore, a detailed column study of heavy metal ion removal from wastewater would be carried out. Both industrially and commercially, adsorption is carried out in a packed column using activated carbon. Furthermore, the batch adsorption study is applicable only to laboratory or small scale industries, and not for large scale and commercial applications.

In the Indian context, there are a lot of unexplored agricultural wastes available, which possess high enough adsorption capacity, and can be utilized for the treatment of different industrial wastewaters. These waste materials can be surface modified by physical or chemical methods to prepare more efficient adsorbents, which can serve as better alternatives to the commercial activated carbon.