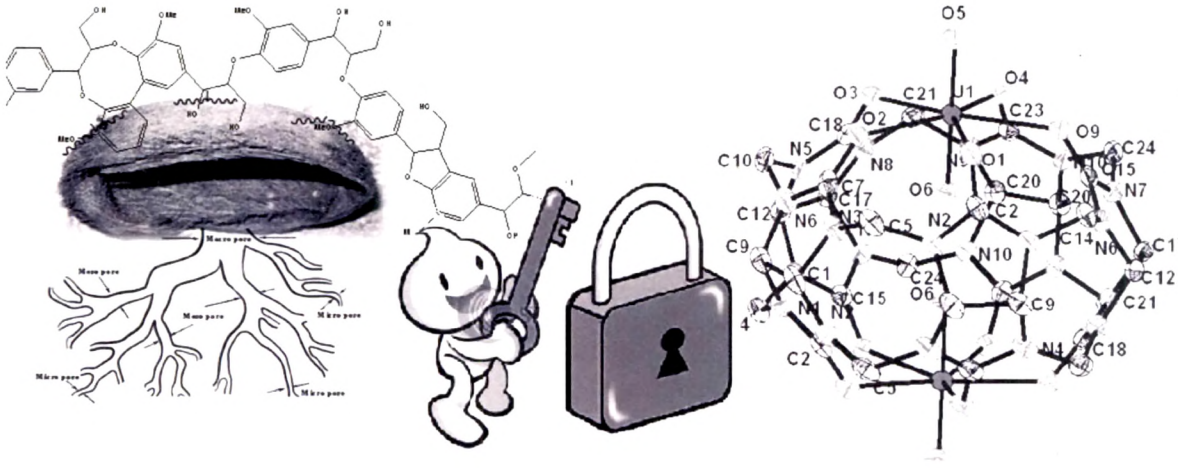
Chapter 9

Conclusions



Palm shell powder (PSP) was modified by either charring with sulfuric acid (APSP) or modifying it with formaldehyde (MPSP). A series of adsorbents were prepared from APSP by steam (SAPSP) and persulfate (PAPSP) treatment at 140°C or thermal activation at 900°C (9AAC). The materials showed some interesting properties.

- APSP, SAPSP and PAPSP were found to have iodine values of 342.5, 199.8 and 299.7 mg/g respectively and significant pore size in spite of their small BET surface areas suggesting high adsorption capacity.
- FTIR, XPS and ^{13}C NMR spectral data indicate that carboxyl, ether, alcoholic, hydroxyl and amino functional groups may be available for metal binding in PSP, MPSP, APSP, PAPSP and SAPSP.
- The presence of aldehydic groups along with etheric linkages of ligno-cellulosic moiety in higher numbers in PSP and MPSP is also indicated.
- Furthermore the number of oxygen containing functional groups were also found to increase with acid treatment and oxidation, the order being SAPSP>PAPSP>APSP> MPSP>PSP>9AAC.

This led us to evaluate their efficacy towards the removal of several toxic and heavy metal ions like copper, cadmium, zinc, mercury, chromium and uranium.

- The adsorption capacity increased in the order Cr>Cd>U>Zn>Hg>Cu for PSP; Cr>U>Zn>Cd>Cu>Hg for APSP; Cd>Cr>U>Zn>Cu>Hg for SAPSP; Cd> Cr>Zn>U>Cu>Hg for PAPSP; Cd>Cr>U>Zn>Cu>Hg for 9AAC and Cr>Zn>U>Cd>Hg>Cu for MPSP. The low adsorption capacity of mercury could be due to the soft nature of mercury and the hard nature of the dominant carboxyl groups available for binding.
- Column studies have been performed and the breakthrough capacities obtained. However, studies have not been done for optimisation of various parameters like flow rate, bed height had not been done as well as the effect of concentration of the adsorbates has not been studied. These studies would provide useful information for designing pilot- and full scale columns for water and wastewater treatment facilities.

- The materials were found to have adsorption capacity either comparable to or better than those reported in literature.

It is observed that the adsorbents were effective towards adsorption of the metal ions under study in a wide pH range (the amount remaining in solution would be below prescribed limits) in contrast to most of the adsorbents reported in literature due to the presence of functional groups with different pK_a values. Furthermore Cr^{3+}, Cr^{6+} were found to adsorb quantitatively at acidic pH which would be advantageous in the treatment of effluents containing these metal ions which are usually acidic. This is in contrast to the reports in literature where the adsorption of Cr^{3+} was found to be drastically low in acidic pH and even reduced Cr^{6+} was reported to come back into solution. Uranyl ions could be removed effectively in both acidic and alkaline conditions which would be of great advantage as uranium is present in both acidic and alkaline effluents of the nuclear industry.

XPS analysis of metal loaded adsorbents provided interesting results .Mercury loaded PSP showed the presence of elemental mercury which increased the adsorption capacity of mercury in PSP. Chromium (VI) was found to get reduced to Cr(III) on the adsorbents under study while U(VI) was getting reduced to U(V) and U(IV).

- The advantage of the reduction processes being, more number of carboxyl groups are generated leading to greater adsorption capacity as observed for uranium and chromium as well as mercury in the case of PSP.
- Cr (VI) was found to get partly reduced to Cr(III). Studies need to be done to check whether complete reduction would be possible with further change in conditions. The chromium (III) containing adsorbents could then be used as reductant for the preparation of basic chromium sulfate (tanning agent). Another alternative would be to identify conditions where chromium could remain on the adsorbate as Cr(VI) which would be useful in chromate recovery processes in electroplating industries. The stability of the sorbent against oxidation by chromate, the elution efficiency of bound chromate, and the regenerability of chromate-loaded sorbent would be equally relevant considerations.
- The reduction of U(VI) to U(V) and U(IV) by the adsorbents under study is unique and highly advantageous in the remediation of uranium (VI) containing waste waters.

Multiple mechanisms seem to be involved in the adsorption process by the adsorbents under study. The main mechanisms being hydrogen-bonding, physisorption, chemisorption, ion exchange and precipitation. Furthermore in the case of chromium(VI) and uranium(VI) adsorption followed by reduction seems to be a predominant mechanism. However, further studies are needed to find whether reduction is the rate controlling step.

Multicomponent studies have been done by the use of synthetic binary, ternary and quarternary mixtures containing the metal ions under study. The results were encouraging. However, the real samples would not only contain a number of metals but also natural organic matter and other organic pollutants. The effect of these pollutants on the adsorption of metal ions has to be studied.

The study indicates that though palm shell based adsorbents are quite effective in the removal of metal ions, selectivity could not be achieved either during adsorption or during desorption process. The adsorbents can definitely serve as a potential alternative for water treatment though further studies are needed as discussed above. However they cannot be applied for specific recovery of a particular metal. But they can be applied for recovery of metals from specific effluents. Though the ability of the adsorbents for the removal of uranium in the presence of iron and cesium has been demonstrated, further work needs to be done in the presence of other constituents which are usually present in nuclear plant effluents before coming to any conclusion regarding the efficacy of the adsorbents in this direction. The results obtained in this study definitely show that palm shell has some unique constituents which results in its reduction of mercury and uranium which is in contrast to the results reported by other plant based materials. Studies related to analysis of palm shell constituents (sugar palm) in detail are not available in literature. Studies in this direction would be interesting and useful.

Chitosan barbital based adsorbents were prepared and were evaluated for their adsorption potential towards inorganic mercury, methyl mercury and phenyl mercury. Speciation was achieved by sequentially eluting inorganic, methyl and phenyl Hg^{2+} using 0.1N $HClO_4$, 0.015N NaCl and 0.05 N EDTA respectively using barbital grafted chitosan. BCL showed better

selectivity for mercury in synthetic mixtures containing copper, cadmium and zinc as compared to C, BC and CL in the concentration range studied.

A novel fluorescent complex {(UO2)2(CB5)}(NO3)8·3H2O (U2CB5) was obtained from cucurbit[5]uril and uranyl nitrate under ambient temperature conditions. The crystal structure revealed that two uranyl ions are coordinated to the two open portals of CB5 giving a closed molecular capsule, which further connected through CB5 molecules to give two-dimensional frameworks.The UCB5 complex was oligomerised and a non-covalent method was used to graft uranyl complexed cucurbituril oligomer onto PSP which led to a rigid, cost-effective ion imprinting oligomer selective for uranium. However, it would be interesting to study the fluorescent properties of the uranyl containing polymer. It could definitely be showing some interesting properties as compared to the U2CB5 complex and could show potential as a sensor. The U2CB5 complex could also be tested for its potential as a catalyst, for instance decomposition of hydrogen peroxide.