CHAPTER ONE

1.0 Introduction

1.1 General

The continually increasing demand for water for beneficial purposes has forced man to assess and examine water reuse technologies more seriously than ever. Regardless of origin, industrial wastewater, after proper treatment, represents another ample and reusable water source. Water pollution due to toxic heavy metals has been a major cause of concern to scientists and engineers. Several mishaps due to heavy metal contamination in aquatic environment increased the awareness about heavy metal toxicity. Public awareness for pollution caused by heavy metals is now worldwide. Among the many heavy metals, lead (Pb), mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), zinc (Zn), and copper (Cu) are of most concern, although the last three metals are essential nutrients for animals and human. They find wide spread usage in industries. These metals enter the environment wherever they are produced, used or discarded. They are very toxic because as ions or in compound forms, they are soluble in water and may be readily absorbed into living organisms. After absorption, these metals can bind to vital cellular components such as structural proteins, enzymes, and nucleic acids, and interfere with their normal functioning. In humans, some of these metals even in small amounts, can cause severe physiological and health disorders.
The compound of chromium, especially hexavalent chromium, are known to be detrimental to human beings, plants, animals and aquatic life (Stomberg, 1984; Tondon, 1982). Over exposure of chrome workers to chromium dust and mists will cause irritation and corrosion of skin, respiratory track and probably lung carcinoma (Hayes, 1982). Ingestion may cause epigastric pain, nausea, vomiting, severe diarrhea and hemorrhage (Browning, 1969). On the other hand, trivalent chromium has been found to be an essential trace element in the human diet and deficiency in trivalent chromium has been linked with poor sugar metabolism (Katz, 1991).

Naturally occurring chromium is chiefly in the form of chromites (Cr₂O₃) or chrome-ore (FeO-Cr₂O₃). Chromium compounds are widely used in the electroplating of metal for corrosion resistance, plastic coating of surfaces for water and oil resistance, leather tanning and metal finishing, and in pigments and wood preservative etc. and consequently discharging hexavalent chromium bearing wastewater. Anthropogenic production of hexavalent chromium in smaller amounts is through drilling mud, rust and corrosion inhibitors, textiles and toner for copying machines (Sujatha, et al., 1995). Hence it is a challenging task for the industrialists and environmentalists to dispose off waters containing heavy metals safely and effectively.

There are many techniques for the treatment of chromium bearing effluents, some of which are well established that have been in practice for decades such as precipitation, co-precipitation (Patterson and Passino, 1987), and concentration. These processes simply remove chromium from wastewater by reduction (Shen and Wang.
1995), coagulation and filtration. Although these technologies are quite satisfactory in terms of purging chromium and other heavy metals from wastewater, they produce solid residues containing toxic compounds whose final disposal is generally by land filling. It involves high costs and has possibility of ground water contamination. From environmental point of view, removing pollutants from liquid wastewater does not solve problem but transfer it from one phase (usually liquid) to another phase (usually solid). There is possibility that the presence of organic ligands and/or acidic conditions in the environment increases Cr (III) mobility, and also MnO$_2$, in the soil, could oxidize Cr (III) to more toxic and mobile Cr (VI) forms (Heary and Ray, 1987). Accordingly, the practice of land filling and land application of chromium contaminating sludge should be discouraged.

In recent years, the use of adsorption techniques for the removal of heavy metals has received global attention (Raji, et al., 1998; Ajmal, et al., 1995, 2000; Huang, et al., 1975). Chemical contaminants at low concentrations are difficult to remove from the wastewater. Chemical precipitation, reverse osmosis and other methods become inefficient when contaminants are present in trace concentrations. The process of adsorption is one of the few alternatives available for such situations (Huang and Morehart, 1991). Several researchers have been working on the heavy metals removal. However, most of them used commercially available activated carbon. The high cost of activated carbon and its loss during the regeneration restricts its application. Thus there is need to undertake studies to substitute the costlier commercial activated carbon with the unconventional, low cost and locally available agricultural waste adsorbents (Bailey, et al., 1999; Brown, et al., 2000). India is an agricultural country and generates
considerable amount of agricultural wastes such as sugar cane bagasse, coconut jute, nut shell, rice straw, rice husk, waste tea leaves, ground nut husk, crop wastes, peanut hulls, compost wastes etc. Studies on these materials could be beneficial to the developing countries and could be easily incorporated in development of appropriate technologies. Recently a few researchers have explored the possibility of using agricultural waste adsorbent for the Cr (VI) removal (Gang, et al., 1999; Deo, et al., 1992; Huang, et al., 1975; Periasamy, et al., 1991; Ayub, et al., 1998, 1999, 2001, 2002; Drake, et al., 1996; Shukhla, and Sakhardane, 1991; Weber, 1996; Chand, et al., 1994; Siddiqui, et al., 1994; Camino, et. al., 2000, Yaishya and Prasad, 1991).

The present study is to evaluate the heavy metal removal potential of agro-waste materials such as coconut shell, neem bark (Azadirachta indica) and raw sugar cane bagasse in the treatment of wastewaters. The effects of pH, contact time, adsorbent dose, concentration of metal, particle sizes and temperature were studied. The samples of the adsorbents were characterized before and after adsorption. The column studied were made to get the data to design a continuos system and to compare it with the batch performance. Electron microscopic technique was used to characterized the surface of the adsorbent. Various adsorbents were used to determine the removal potentials of different agricultural wastes. Thermodynamic nature of the process was also studied.
1.2 Chemistry of Chromium

Chromium is highly active transition metal which exists in a number of oxidation states which exhibit a wide range of stability. Thermodynamically, the reduced form of chromium, Cr (III), is the most stable in both acid and basic solutions as evidenced by the reduction potential ($E^0$) diagrams presented in Figure 1.

$$\frac{1}{2}Cr_2O_7^{2-} + 2e^- + 2H^+ \rightarrow 2Cr^{3+} + H_2O$$ 
(Reaction 1.1)

$$\frac{1}{2}CrO_4^{2-} + 2e^- + 4H^+ \rightarrow Cr^{3+} + 2H_2O$$ 
(Reaction 1.2)

Positive $E^0$ values denote that the reaction will proceed spontaneously ($\Delta G^0$) to the right (reduction) under standard conditions, whereas, negative $E^0$ values indicate that the oxidized species is favored. Cr (III) is the most stable because it would require significant energy to reduce Cr (III) to Cr$^0$ or oxidize Cr (III) to Cr (VI) (Nieboer and Jusys, 1988).
The stability of the various chromium species is dependent upon the various reduction, oxidation and pH conditions. The stable domains for various chromium species in aqueous system as affected by the oxidation potential ($E_h$) and pH (Landrigan, 1975). Under the pH (< 3), temperature (20-30°C) and reducing - oxidizing conditions commonly found in industrial wastewaters, the predominant species are bicarbonate, HCrO$_4^-$, dichromate Cr$_2$O$_7^{2-}$ and Cr$^{13}$. It is interesting to note that the divalent chromium ions, Cr$^{3+}$, may be found in extremely reducing environment. The concentration distribution between HCrO$_4^-$ and Cr$_2$O$_7^{2-}$ is largely governed by the total Cr (VI) present. The fraction of Cr$_2$O$_7^{2-}$ only becomes significant at high concentration of total Cr (VI) (Stumm, 1970).

1.2.1 Use of Chromium

Chromium is used to increase resistance & durability of metals by chrome plating. Chromium based pigments are used for floor covering products, paper, cement, and asphalt roofing. The other usages of chromium are in fabrication of alloys, colouring of glass, ferrous as well as non-ferrous, production and processing of insoluble salts, chemical intermediates; use in textile industry in dyeing, silk treating, printing, leather industry tanning and in photographic fixing baths. Catalysts for halogenation, alkylation, and catalytic cracking of hydrocarbons and fuel additives and propellant additives.
Chromium and its compounds are used in making special alloys protective coatings on metal; magnetic tapes; and pigments for paints, cement, paper, rubber, floor covering and other materials. In medicine, chromium compounds are used in astringents and antiseptics.

1.2.2 Disposal of Chromium

It has been routine practice to use land treatment or burial (sanitary landfill) methods to dispose off the chromium contaminated waste generated from the treatments. However, this practice is subjected to significant revision taking into consideration the underground water contamination. Disposal of chromium wastes from the electroplating operation can be divided into; (1) discharge of liquid effluents directly into the water courses, (2) discharge into municipal sewers.

The sludge generated by the precipitation process is generally voluminous and difficult to dewater. The removal of sludges from the wastewater is normally done by the gravity settling in a clarifier. Sludge generated by precipitation typically contains 0.5-3.5 % solids. Freshly precipitated sludge have the characteristics of a very low specific gravity, which makes effective settling difficult without long clarifier detention time.

Ion exchange is used to remove either trivalent or hexavalent chromium from wastewater. This method is preferred when chromium is to be recovered for reuse. It
performs better in the pH range of 4.5 to 5.0. Ion exchange is an attractive method for the removal of small amount of impurities from dilute wastewaters, or the concentration and recovery of expansive chemicals from segregated concentrated wastewaters. The limited capacity of ion exchange systems mean the relatively large installations are necessary to provide the exchange capacity needed between regeneration cycles. It is an expansive methods and needs additional treatment unit for the spent resin regeneration. Wastewater treatment consisting of chromium reduction followed by ion exchange would normally not be economical.

Clarification, with or without sludge conditioning, is not completely effective in solid – liquid separation. Some of smaller floc will escape even the most effectively designed clarifiers. In order to treat increasingly stringent effluent standards, adsorption has shown potential for treating chromium bearing low concentration wastes as a polishing sludge free treatment technology.