Spring 2008

Removal of heavy metals from electroplating wastewater using rice husk and coconut coir

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Recommended Citation

Mathew, Frency, "Removal of heavy metals from electroplating wastewater using rice husk and coconut coir" (2008). *Masters Theses*. 5019.
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REMOVAL OF HEAVY METALS FROM ELECTROPLATING WASTEWATER USING RICE HUSK AND COCONUT COIR

by

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A THESIS

Presented to the Faculty of the Graduate School of the

MISSOURI UNIVERSITY OF SCIENCE AND TECHNOLOGY

In Partial Fulfillment of the Requirements for the Degree

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

2008

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ABSTRACT

Heavy metal toxicity due to industrial wastewater has been a threat to the environment for the past many decades, especially in the developing countries such as India, China and Thailand where cost effectiveness of the removal process is a major factor.

In this research, the effectiveness of two natural adsorbents, rice husk (RH) and coconut coir (CC), which are cheaply available in these countries for the removal of heavy metals from electroplating wastewaters were studied. Batch adsorption and desorption studies were conducted on these adsorbents with Cr (VI), Cr (III), Cd (II), Cu (II) and Ni (II). The effectiveness of the adsorbents were studied in the pH range from 2-12. The adsorption mechanisms were also studied.

RH showed a maximum removal efficiency of 99.5 % for Ni (II), 80.0 % for Cd (II), 72.8 % for Cr (VI), 56.2 % for Cr (III) and 40.0 % for Cu (II). CC showed 99.5 % for Ni (II), 92.8 % for Cr (VI), 50.7 % for Cr (III), 40.5 % for Cd (II) and 40.4 % for Cu (II). Comparing the two adsorbents, CC was found to be more efficient for metal ion removal than RH. Desorption studies showed that when Cr (III), Cd (II) and Cu (II) are the adsorbates, the RH and CC can be regenerated and reused. For the other metals only partial regeneration for RH and CC was possible.

ACKNOWLEDGEMENTS

I would like to express my deep and sincere gratitude to my advisor, Dr. Douglas K. Ludlow and co-advisor, Dr. Craig Adams for their patience, time, cooperation and kind help without which this project would have been very difficult to complete. I would also like to thank Dr. Kimberly Henthorn for being on my committee. I am very thankful to Honglan Shi for all the help she has given me in the Environmental Research Center (ERC) lab. I also thank all my lab buddies at ERC for being nice and friendly.

My deepest gratitude goes to my father, mother and brother for their unflagging love, prayers and support. I will never forget the courage and strength I received from my best friends, Ajay, Jincy and Merene, when things were not going on so well.

Finally, and most importantly I would like to thank God, for it is under his grace that we learn, live and flourish.

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1. LITERATURE REVIEW

1.1. INTRODUCTION

Electroplating or the metal finishing industry plays an important role in the development of many metal manufacturing and other engineering industries in the world. While the electroplating operations have become an integral part of the engineering industries there has been a steady growth of independent and small to medium scale electroplating industries, mainly in the developing countries of South East Asia like India, Thailand and China.

In India, there are over 50,000 large, medium and small electroplating units scattered in urban areas. The electroplating industry is mainly represented by small scale units having distinct features such as tiny, family owned units; practicing old and obsolete technologies having unskilled or semiskilled workers; located in unplanned and unauthorized areas with lack of industrial infrastructure facilities; and working in small shop areas [1].

1.2. ELECTROPLATING PROCESS

Electroplating is the process of depositing a coating having a desirable form by means of electrolysis i.e. by the use of electricity. Its purpose is generally to alter the characteristics of a surface so as to provide improved appearance, ability to withstand corrosive agents, resistance to abrasion, or other desired properties or a combination of them, although occasionally it is used simply to alter dimensions. The process involves the dissolving of metal at the anode and depositing at the cathode by passing electricity through the electrolytic bath. Some metals which are commonly used for electroplating are copper, chromium, nickel, lead, cadmium, tin, zinc, brass or combinations of them. Platers immerse objects into a series of chemical baths in order to change their surface conditions. The numbers of tanks and their chemical makeup differs based on the desired result and every plating plant is different and thus is the constituents of the wastewaters. The electroplating process involves mainly four steps: cleaning, plating, rinsing and drying.

1.2.1. Cleaning. The metal to be plated should be pretreated before it can be plated. The pretreatment includes degreasing and pickling which are done to remove the grease, oil, rust or scale which will be present on the surface of the metal surface. Grease on the metal surface comes from the machining, polishing and the preservation steps of the metal. Degreasing is the process that removes oil, grease and solid dust particles from metal surfaces. Even though there are greases of different nature such as organic, petroleum or mineral oil grease, and each of them needs to be degreased with different chemicals, the most commonly employed method is emulsification with metals cleaners. Metal cleaners are solutions which contain mixtures of sodium carbonate, caustic soda, trisodium phosphate, sodium silicate, sodium cyanide and borax.

Treatment of metallic surfaces in order to remove impurities, stains, rust or scale with an acidic solution is called pickling. The two acids commonly used as pickling liquor are hydrochloric acid and sulphuric acid.

1.2.2. Plating. Once the metal is cleaned, it is ready to be plated with the desired metal. Wooden or steel vats are used according to the nature of the plating bath. Plating operations are always wet. The pickled metals are placed in these vats containing the metal which is to be plated onto the base metal. The electroplating bath contains metal salts, alkalis and other bath control compounds in addition to plating metals like copper and nickel. The base metal is plated with the respective metals by the process of electrodeposition where the material to be plated acts as the cathode is dipped in the electroplating bath which is the anode. In electroplating, metal ions supplied by the dissolution of metals from anodes or other pieces are reduced on the work pieces (cathodes) while in either acid, alkaline, or neutral solutions. The electroplating bath contains metal salts, alkalis and other bath control compounds in addition to plating metals like copper and nickel [2].

1.2.3. Rinsing. After the plating process, the plated metal is rinsed with water to make sure that the plated surface will be free of any spots from the plating. This rinsing may be done a couple of times. The surface is first dipped in a stationary cold bath and then rinsed in a running water bath where it can be either a cold wash or a hot wash. In the last rinse, commonly, deionized water is used.

1.2.4. Drying. After plating and rinsing the plated metal needs to be dried. There are various methods employed for drying in electroplating industry such as placing the metal in a heated oven or hanging the piece in a blast of hot air or high pressure compressed air jet. Another method for drying small plated articles is to place them in a centrifuge basket to throw the water off by centrifugal force. Hot sawdust is also sometimes used where the sawdust absorbs moisture and also gives a slight degree of polish to the plated metal and also removes any leftover stains [3].

1.3. WASTEWATER FROM ELECTROPLATING INDUSTRY

The electroplating industry consumes and discharges large volumes of wastewater. This effluent is very hazardous, containing heavy metals such as nickel, chromium, copper, zinc, lead and silver as well as cyanides, hydrogen sulfides, ammonia, oil and grease and suspended solids. The characteristics of electroplating wastewater differ from plant to plant depending on the type of plating and the method employed for their treatment.

1.3.1. Characteristics of Electroplating Wastewater. After few days or weeks, plating contents and acids used in the pretreatment and other steps get contaminated and need to be disposed for maintaining the quality of plating. Most of the wastewater from the electroplating plant comes from the rinse waters and the batch solutions used for plating. The batch solutions have a high concentration of contaminants whereas the rinse waters are comparatively dilute. In small shops, there is typically one central swill for rinsing the articles from different stages in the process and they get contaminated quickly. These discharges will be very dilute. The wastewater from the pretreatment step mainly contains the cleaning solution and all the spent alkaline solutions containing suspended solids, soaps, grease and oil. These spent alkaline solutions are held in steel vats for controlled discharge. They have a pH of around 12 and before discharge they are mixed with acid water to lower the pH.

Wastewater from pickling includes acidic rinse water, metallic salts and waste acid. It usually has a pH below 2.5. The rinse water from the pickling stage is acidic and it is stored in tanks for controlled discharge. It is more frequently discharged compared to the other wastes. Metal wastes from plating baths include rinse waters from copper, zinc, nickel, cadmium and lead vats. All these baths are seldom used together. These metals are present in the wastewater in ionic form and are extremely toxic. The composite plating waste may be acidic or alkaline depending on the type of baths that are used. The effluent concentrations depend on various factors such as surface area, shape of the article, thickness of the solution and drain time.

1.3.2 Environmental and Health Problems. Accumulation of heavy metals in the food chain and their accumulation in nature is a common phenomenon. There are copious amounts of water being discharged from these electroplating units without any pretreatment before entering the water bodies. These wastewaters mainly contain heavy and transition metals, cyanides, oil and grease and suspended solids at levels that are hazardous to the environment and human health. They contain organic matter which depletes the oxygen content from the water bodies and they also have inorganic matter that make the water body unfit for further use and encourage undesirable growth of plants in the water bodies. The acids and alkalis in the electroplating industrial discharge make the receiving stream unsuitable for the growth of fish and other aquatic life. The heavy metallic ions such as chromium, nickel, zinc, lead, silver, cadmium, copper, mercury and other toxic substances like cyanide, sulphide, ammonia, chloramines, cause damage to the flora and fauna. Oil and grease and other floating substances render the streams unsightly and interfere with their self purification [4]. Electroplating wastewater is variable in character and alkaline in nature. In India, in places with scarcity of water, people go to the rivers for bathing and washing. These wastewaters give off a very bad smell which makes it very difficult for people who live near these polluted waterbodies. The color of wastewater imparts visual pollution and persists for long distances in river streams and decreases the recreational capacity of the stream. It also causes disturbed penetration of sun rays which in turn can retard photosynthesis activity [1].

1.3.3. Effluent Standards. Until the 1950's, the electroplating industrial wastes were discharged into the drains without any prior treatment. When the awareness came about the high toxicity and corrosiveness of plating wastes streams, the authorities took action to make sure that the plating facilities pretreated their wastewater prior to discharge and they released national standards for the acceptable limits for the various metals and compounds before they can be discharged to the waterbodies. Table 1.1 shows the Indian national standards for effluent discharge which was released in 1974 [5] and Table 1.2 shows the standards set for the electroplating industry by United States Environmental Protection Agency (USEPA) [6]. As seen from the tables, the effluent limits set by USEPA are much lower than the standards set by the Indian Government for electroplating industries.

Even though the electroplating industry uses less water in comparison to the other industries, their effluents are far more toxic. Electroplating wastewaters contain heavy metals, cyanides and suspended solids which need to be treated before disposing into the rivers because they are hazardous to the aquatic life and humans and pose a serious threat to the environment. The tolerable limits of these heavy metals and other constituents in water and land environment are in general very low. The heavy metals such as chromium, cadmium, mercury, nickel, lead and cyanides are the constituents which need careful treatment because of their toxic effects.

Table 1.1. Indian Standards for Maximum Permissible Limits for Industrial Effluent Discharges (in mg/L) [5].

Parameter	Indian Standards: 2490 (1974), Inland surface waters	Indian Standards: 3306 (1974), Public sewers	Indian Standards: 3307 (1974), Use for irrigation
pH	5.50-9.00	5.50-9.00	5.50-9.00
BOD* (for 5 days at 20 ^{0}C	30.00	350.00	100.00
COD**	250.00	--	--
Total Dissolved Solids (TDS)	2100.00	2100.00	2100.00
Oil and Grease	10.00	20.00	10.00
Cyanides	0.20	2.00	0.20
Cadmium	2.00	1.00	--
Chromium (VI)	0.10	2.00	--
Copper	3.00	3.00	--
Lead	0.10	1.00	--
Mercury	0.01	0.01	--
Nickel	3.00	3.00	--
Zinc	5.00	15.00	--

BOD* - Biochemical Oxygen Demand

COD** - Chemical Oxygen Demand

Table 1.2. United States Environmental Protection Agency Electroplating Effluent Standards .

Parameter	Daily maximum (mg/L)	4 day average (mg/L)
Total Cadmium	1.2	0.7
Total Chromium	7.0	4.0
Total Copper	4.5	2.7
Total Lead	0.6	0.4
Total Nickel	4.1	2.6
Total Zinc	4.2	2.6
Total Silver	1.2	0.7
Cyanides	1.9	1.0
Total toxic organics	2.1	-

1.4. HEAVY METAL TOXICITY

Heavy metals are metallic elements which are very toxic and have a high atomic weight and a relatively high density. The body needs many trace element heavy metals in small concentrations, but there are another 12 poisonous heavy metals, such as lead, mercury, cadmium, chromium and nickel which are bad for the body. These poisonous metals affect our enzyme systems and can also affect the metabolism of the body. They are highly toxic and can cause damaging effects to our body even at very low concentrations. Exposure to these elements may cause immediate as well as delayed adverse health effects like the risk of dermal damage, respiratory problems and several kinds of cancer. They tend to accumulate in the food chain and in the body. Once they enter our body they get stored in soft and hard tissues which can cause chronic health effects [7].

Environmental contamination and human exposure to heavy metals is a serious growing problem throughout the world. As the use of heavy metals has tremendously increased in the industrial process, humans are being exposed to them more and are having a greater risk of health effects that they cause.

For this project we considered five toxic metals which are chromium (VI), chromium (III), cadmium (II), copper (II) and nickel (II). The toxic effects each of these heavy metals are discussed below.

1.4.1. Chromium. Chromium is one of the 129 priority pollutants listed by the Environmental Protection Agency (EPA) [8]. Chromium has two main oxidation states: [Cr (III)] and [Cr (VI)].

Chromium (III) compounds are stable and occur naturally in the environment and are essential nutrients in our diet. Our body needs a very small amount of it for maintaining the glucose, lipid and protein metabolism in our body. On the other hand, Cr (VI) is toxic, non-biodegradable and is a carcinogenic [9].

Although Cr (III) is less toxic than Cr (VI), long term exposure to a high concentration of Cr (III) may cause poisoning symptoms like allergic skin reactions. Acute exposure causes nausea, vomiting, shock and coma and can be fatal. It can also cause kidney and liver damage. Chronic exposure causes respiratory effects like ulcerated performation of the nasal septum, irritation of mucous membranes and general bronchospasm. Chromium (VI) which is more toxic is associated with lung cancer and kidney damage [10]. In aquatic organisms, Cr (VI) has a high potential for bioaccumulation which means it accumulates in their bodies and cause chronic effects.

Because of the toxic nature of Cr (VI), the discharge of Cr (VI) is regulated to <0.05 mg/L to surface waters and 0.1 mg/L to inland surface waters according to the USEPA, whereas the total chromium (containing Cr (III), Cr (VI) and other forms of chromium) is regulated to be discharged at < 2 mg/L [11].

1.4.2. Cadmium. Cadmium is also listed by the EPA as one of the 129 priority pollutants [8]. All cadmium compounds are potentially harmful or toxic. Cadmium acts as a cumulative poison.

Acute cadmium toxicity in humans often leads to pneumonitis which can be fatal. Signs of acute cadmium poisoning include vomiting, digestive tract irritation, colitis, diarrhea and prostration [12]. The main health effect related with cadmium toxicity is proteinuria which is caused by kidney damage. Studies have proven that cadmium also affects the activities of certain enzymes in the body.

Cadmium mainly accumulates in the kidney and the excretion of cadmium from the body is very slow and it takes about 10-40 years. Long time exposure to cadmium causes lung, kidney and hematopoietic system damage due to build up, fragile bones and anemia [13]. In studies conducted on animals cadmium has shown strong evidence of cancer. There is not much evidence of cancer caused due to cadmium exposure in humans.

Fish and wildlife are greatly affected by cadmium which is very toxic and causes behavioral, growth and physiological problems in aquatic life at low concentrations. Cadmium is the only metal which accumulates with the increasing age of an animal [14].

The discharge of cadmium is regulated to < 2.0 mg/L into inland surface waters in India [15]. The allowable limit of cadmium in drinking water according to World Health Organization (WHO) is <0.003 mg/L and <0.005 mg/L according to the USEPA [16].

1.4.3. Copper. Copper is an essential nutrient for humans and animals, with a Recommended Daily Allowance (RDA) of 0.9 milligrams per day [17]. Copper is a component of many body proteins.

Acute exposure to copper causes gastrointestinal effects such as nausea, vomiting and diarrhea. Two grams or more of copper dose can cause serious effects such as vascular injury and hemolytic anemia, resulting in severe renal and liver damage which can lead to death [18].

Copper has both acute and chronic effect on aquatic organisms that can result in death. They are known to bioconcentrate in some aquatic species. In mammals, overexposure to copper can damage the liver and kidney [19]. It is the younger fishes that are affected the most by the toxicity of copper. The adult fishes can tolerate small concentrations of copper for small periods of time [20].

1.4.4. Nickel. Nickel is a dietary requirement for many organisms, but may be toxic in larger doses. The human body contains approximately 100 mg of nickel [21].

Acute nickel toxicity effects are gastrointestinal symptoms like nausea, vomiting, abdominal discomfort and diarrhea and neurological symptoms like headache, giddiness, cough and shortness of breath. Many people develop dermatitis upon skin contact with nickel. Nickel salts affect the pulmonary and digestive tract of humans. Exposure to soluble nickel compounds also causes respiratory tract cancer if the dosage exceeds 1 μg of Ni/ L [22].

Chronic health effects of nickel include chronic bronchitis and lung disease which is caused by reduced lung function. Nickel also affects the blood, liver, kidney and immune systems [23]. There is some evidence of lung and nasal sinus cancers in humans. Metallic nickel is teratogenic and carcinogenic to mammals [22].

1.5. VARIOUS METHODS FOR TREATING ELECTROPLATING WASTERWATER

There are many physical, chemical and biological methods that are currently being used for treating electroplating wastewater. Some of the commonly used methods are discussed below.

1.5.1. Chemical Precipitation. This is one of the cost effective ways of removing heavy metals from wastewater. In this method a chemical additive is selected in such a way that it will make the metal that is to be removed from the wastewater insoluble. After the metal precipitates in the solution then it can be easily removed from the water by filtering or settling. Most of the metals are precipitated as metal hydroxides by raising the pH to a neutral or an alkaline level. However, this method is not effective enough to meet the discharge effluent standards. Another problem with this method is that chelated metal ions do not precipitate at all. So, for metal hydroxides more advanced treatments such as reaction with organic or inorganic sulfides are employed. Chemical precipitation uses hydroxide, carbonate or sulphide reagents for precipitation such as lime and soda [24].

The theory of chemical precipitation is a complex one. One of the many disadvantages of this process is that the precipitation process is often left incomplete and there are many side effects related to it. Even though it is a cost effective method for wastewater treatment, it is not efficient enough to meet the discharge limits. Another disadvantage of this process is that it generates large amounts of water rich sludge which needs to be disposed [25].

1.5.2. Coagulation/ Flocculation. Flocculation is one of the widely used method for removing suspended particles from wastewater. It is a process in which the metal to be removed is separated out from the solution as flocs or flakes which can then be easily removed. Flocculation is often preceded by coagulation where, by the addition of a coagulant, substances are aggregated into microscopic particles which then flocculate into larger flocs. In this process the destabilized suspension is mixed very slowly to provide an opportunity for the particles to come into contact with one another and form flocs. The most commonly used coagulants–flocculants in wastewater treatment are aluminum sulphate, calcium oxide, iron (III) chloride, iron (II) sulphate and sodium silicate [26]. These are often used with various coagulant aids, such as synthetic polyelectrolytes (anionic, cationic, or non-ionic polymers), fly ash and clay [27].

The disadvantage of this process is that it has a moderately higher total operation and maintenance cost which is mainly due to sludge handling.

1.5.3. Ion Exchange Method. Ion exchange is a process in which the metal ions are removed from the aqueous phase by the exchange of cations or anions between the exchange medium and the wastewater. The materials used for making ion exchange media are either natural or synthetic organic materials or inorganic polymeric materials. These resins can be regenerated for re-use after their exchange capacity is exhausted.

Even though this is an efficient method for wastewater treatment, it is not that widely used because of its high cost. Another disadvantage of this method is that during the ion exchange process these resins absorb and store all the toxic chemicals which need to be disposed. Large quantities of salt is formed which also need to be taken care of [25].

1.5.4. Electrolytic Deposition Method. This method is mainly used for treating cyanide-containing wastewater. In this process the cyanide wastes are subjected to electrolysis at high temperatures (95°C) for several days. One disadvantage of this process is that the process may not reach completion and some residual cyanide and cyanate remains which need further treatment [25].

1.5.5. Evaporation. Evaporation of plating wastewater has been studied to recover the plating metals. Single stage and multiple stage evaporation have been employed. Because of high cost of equipment this method is not commonly used [25].

1.5.6. Biosorption. This is a biological sorption method used for heavy metal removal from wastewater. Live or dead microorganisms or their derivatives are used in biosorption. In this method the metal ions are complexed by the functional groups present on their outer surfaces through the action of ligands. It is an effective and a cheaper method compared to the other removal techniques [28].

The disadvantages of this process are that it takes a long time for the removal of heavy metals and also that the regeneration of the material for further biosorption is not possible [28].

1.5.7. Activated Carbon Adsorption. Adsorption using activated carbon is one of the most attractive methods for heavy metal removal from wastewater because of its high efficiency in removing metals [29]. This method is not that popular in developing countries because of high initial and operating costs [30].

1.6. ADSORPTION

Adsorption is one of the more effective methods for removing heavy metals from industrial wastewaters. Adsorption is the surface phenomenon of binding molecules or particles in a solution onto a surface. It is also defined as the "increase in concentration of a particular component at the surface or interface between two phases" [31]. The substance that is removed from the liquid phase is called the adsorbate and the adsorbent is the solid, liquid or gas phase onto which the adsorbate accumulates. Atoms at the surface of a solid or liquid are subject to unbalanced forces of attraction which are merely forces acting within the body of the material and are responsible for the phenomenon of adsorption.

Adsorption is mainly of two types: physical adsorption and chemical adsorption. The physical adsorption process does not involve the sharing or transfer of electrons. The interactions are fully reversible enabling desorption to occur at the same temperature and is not site specific. Whereas, chemical sorption involves chemical like bonding onto the surface of adsorbents and is typically an irreversible process. Chemisorption is site specific i.e. the chemisorbed molecules are fixed at specific sites.

For adsorption modeling, there is a need to find the rate determining step of the adsorptive process. Adsorption is a mass transfer operation and the kinetics involved in the adsorption is simple. The adsorption process takes place in three steps: (1) the first step is the transport of the adsorbate from bulk solution to the outer surface of the adsorbent by molecular diffusion which is called external or film diffusion, (2) the second step, known as internal diffusion involves the transport of the adsorbate from the particle surface to the interior sites by diffusion within the pore and migration along the solid surface of the pore, (3) the third step is the adsorption of the solute on the active sites on the interior of the pores [32].

1.7. ADSORBENTS

There are lots of adsorbents that are effective for heavy metal removal from electroplating wastewater. The principal types of adsorbents are activated carbon, synthetic polymeric, and silica based adsorbents. Many of these adsorbents are not used widely because of their high cost. There are numerous small scale plating plants in developing countries such as India, China and Thailand which are facing problems with treating their wastewater before discharging into the drains because none of the wastewater treatment processes that are effective are economical at the small scale. For this reason, the effectiveness of low cost adsorbents for heavy metals removal is being studied widely with the aim of finding cheap natural adsorbents that are easily available and which are effective in removing the toxic heavy metals in the electroplating wastewaters. Studies has been done on natural wastes where materials such as cotton [33], walnut waste [34], peanut skin [35], sugarcane waste and onion hull [36], coffee grounds [37], tea leaves [38], apple wastes [39], wool fiber [40], bark and other cellulosic materials [41, 42, 43, 44, 45, 46, 47], cottonseed hulls, rice straw, soybean hulls [48] and linseed flax [49] have been studied. In general, they present good adsorption capacity. These unconventional natural adsorbents have advantages other than being abundant in nature. Most of them need less prior processing and are waste by-products from some other industry. So, they are an alternative to costlier adsorbents like activated carbon, or synthetic polymers.

In the present study, the two natural adsorbents studied were: (1) rice husk and (2) coconut coir.

1.7.1. Rice Husk. Rice husks are the outer covering of rice grains. They are the by-products of the rice milling industry and comprise 23 % of the rice grain. Developing countries such as China, India, Indonesia, Bangladesh and Thailand are the leading rice producing countries [50]. Rice husk is abundantly available at minimal cost in these developing countries as it is a waste material. It is used as a source of energy for boilers in rice milling factories and also used as a building material, fertilizer and also in some industries. However, the amount of rice husk available is in excess of all these local uses and there are disposal problems [51]. It is a promising adsorbent, as it contains 15-22 % SiO_2 in hydrated amorphous form like silica gel [52] which is a good adsorbent.

1.7.2. Coconut Coir. Coconut coir is a natural adsorbent that is cheap and available in plenty in developing countries such as India and Sri Lanka. They are the world's top two producers, accounting for 90 % of the global coir fiber production [53]. It is also produced in Malaysia, Philippines and Thailand but in lesser quantities compared to India and Sri Lanka.

Coir, cocopeat, coir fiber pith and coir dust are many terms used to describe the material that is produced from coconut husks. Coconut husk is the fibrous layer of the fruit inside the outer shell of a coconut. Coir is produced as a by-product when coconut husks are processed for the extraction of the long fibers from the husk. It is the binding material that comes from the fiber fraction of the coconut husk [54]. The average yield of coir is 80-90 g fiber per kg of husk [55]. The coir pith had been considered a nuisance and disposal problem with little beneficial uses. Over the decades, coir pith piles grew around the coir mills in India and Sri Lanka. It is bio-degradable but takes as long as 20 years to decompose. Lately it has been discovered that it has adsorbent properties and adsorbent studies have been done. Coir is available in bulk or in blocks and have a pH of 5.2-6.8 [56].

In the current study, the removal efficiency of two cheap natural adsorbents, rice husk and coconut coir for heavy metal ions Cr (VI), Cr (III), Cd (II), Cu (II) and Ni (II) from a simulated electroplating wastewater were studied.

2. EXPERIMENTAL MATERIALS AND METHODS

2.1. ADSORBENT PREPARATION

In our study, we used two different adsorbents: rice husk and coconut coir. These adsorbents were selected on their cost effectiveness and ready availability. These were prepared in different ways.

2.1.1. Rice Husk. The rice husk used for the study was purchased from *The Quality Wine and Ale Supply,* Elkhart, Indiana, USA [57]. The characteristics of the rice husk were obtained from the manufacturer and are shown in Table 2.1. They are the outer covering of the long white rice from a farm in Arkansas, USA. These are brown in color with the size of long grain rice. The rice husks were washed with deionized water by mixing it in a shaker for 2 hours. After that, the water was decanted, and the rice husk was then again shaken with fresh water for another 2 hours. This process was repeated at least four times until all the apparent excess material was removed from the rice husks. The cleaned, wet rice husks were then placed on a large glass baking dish and dried in the oven at 125°C for 18 hours. While it was in the oven, it was stirred occasionally. The dried rice husks were taken out and sieved using a 200- mm sieve so that the fines from it were removed. The larger cleaned rice husks particles were stored in precleaned polypropylene bottles and kept air tight to avoid absorption of moisture from the atmosphere. These prepared rice husks were used for the experiments.

Table 2.1. Characteristics of Rice Husk.

Parameter	Value
Moisture (%)	8.75
Ether extract (%)	1.00
Protein (%)	3.12
Crude fiber (%)	37.5
Ash	20.00
Nitrogen free extract (%)	29.63
Loss on ignition (%)	71.00
Nitrogen (%)	0.05
Silica and other insolubles (%)	18.80
Oxides of iron and aluminum (%)	0.22
Calcium carbonate (%)	0.42
Magnesium carbonate (%)	0.12
Total phosphate as P_2O_5 (%)	0.32
Potash as K_2O (%)	0.12

2.1.2. Coconut Coir. The coconut coir used for the study was obtained from coconut coir bricks imported from Sri Lanka by *The Lazy Gardener*, Whittier, California, USA [58]. The coir bricks were dipped in water and they separated out to a small brown hairy substance. The soluble and colored particles were removed by shaking with deionized water for 2 hours. The water was then decanted and again mixed with fresh water. The washings were repeated until the water became colorless. This wet coir was transferred to a glass baking dish and kept in the oven for drying at 125°C for 16 hours. The dried coir was sieved using the fraction between 350-850 μm and stored in precleaned airtight polypropylene bottles. This material was used for all the experiments.

2.2. ADSORBENT CHARACTERIZATION

The surface areas and pore volume of the adsorbents were measured by the BET method (Brunauer Emmett Teller nitrogen adsorption technique) [59] using a Quantachrome Instruments Autosorb-1 Surface Area Analyzer, USA.

2.3. REAGENTS

All reagents were of analytical grade and deionized water from a Milli-Q system (Millipore S.A., Molsheim, France) was used throughout the experiments. The chromium nitrate, sodium chromate, copper chloride, nickel chloride and cadmium chloride used for preparing stock solutions were of the analytical grade. The other chemicals used were sodium nitrate, sodium hydroxide and 67-70 % assay nitric acid. All of these were purchased from Fisher Scientific, New Jersey, USA.

1 M HNO_3 and 0.5 M NaOH solutions were prepared and used for adjusting the pH of the solution. All pH measurements were carried out using a Corning 430 pH meter. Sodium nitrate buffer solutions having ionic strength of 0.05 M were prepared by dissolving 4.2495 g of $NaNO_3$ granules in 1000 ml of deionized water.

2.3.1. Preparation of Stock Solutions. The synthetic wastewater solutions for each of the metals were prepared from analytical grade chemicals. The stock solutions for chromium (III), chromium (VI), cadmium (II), copper (II) and nickel (II) were prepared from $Cr\ (NO_3)_3 \cdot 9H_2O$, Na_2CrO_4, $CdCl_2$, $CuCl_2 \cdot 2H_2O$ and $NiCl_2 \cdot 6H_2O$, respectively. The stock solutions were prepared by dissolving the exact quantity of the chemicals in deionized water to obtain 5866.67 mg of metal/L of the solution. The solutions were diluted to the required concentrations for the experiments. Throughout our study, we used a nominal metal ion concentration of 20 mg/L of the metal solution after dilution.

2.3.2. Preparation of Standard Solutions for Calibration Curves. Standard solutions of chromium, cadmium, copper and nickel were prepared from the 1000 mg/L reference solutions suitable for flame atomic absorption spectrometry analysis which were purchased from Fisher Scientific, New Jersey, USA. These standards were diluted to the concentrations ranging from 0.1 mg/L to 50 mg/L and stored in polypropylene bottles for use.

2.4. ANALYSIS OF METAL IONS

A Flame Atomic Absorption Spectrophotometer Perkin-Elmer 3110 model (Norwalk, Connecticut, USA) was used to determine the concentrations of Cr (VI), Cr (III), Cd (II), Cu (II) and Ni (II) in the aqueous solution at wavelengths of 357.9, 228.8, 324.8 and 232.4 nm, respectively. All these metals were analyzed using the air-acetylene flame and the respective hollow cathode tubes which were purchased from Perkin-Elmer (USA) were used. Measurements were recorded when three repeatable readings were obtained. Metal ion concentrations were determined in reference to the appropriate standard metal ion solutions.

2.5. BATCH ADSORPTION STUDIES

The adsorption experiments were all carried out by a batch technique at ambient temperature (23±1°C). A S/L ratio, which is the ratio of the mass of the adsorbent to the volume of the buffer solution added, of 1:30 was used. For each experimental run, a fixed amount of the adsorbent (3.67 g) was massed on a Metler Toledo balance and transferred into 125 ml polypropylene bottles which were numbered and kept. Into each of these bottles 110 ml of 0.05 M $NaNO_3$ buffer solution was added. The metal ion concentration of the stock solution prepared was measured using the Atomic Absorption Spectrometer. Each of these bottles was then spiked with 375 µL of 5866.66 mg/L of this metal stock solution. The initial pH values of each of the bottles were adjusted using 1 M HNO_3 and 0.5 M NaOH to an initial pH in the range of 2-12 at an increment of one unit using a Corning 430 pH meter. The volume of the acid or base needed to adjust to the initial desired pH was recorded. Table 2.2 shows the composition in each bottle that was prepared.

After adjusting the pH, the bottles were tightly sealed and kept in a mechanical shaker at low speed for 24 hours. After 24 hours, the bottles were taken from the shaker and the final pH was recorded. A 10 ml aliquot of solution was filtered from each of the bottles using a latex free syringe and 25 mm syringe filter (0.45 µm, nylon) and transferred into 15 ml polypropylene tubes and capped. The filtrate was analyzed on an Atomic Absorption Spectrophotometer to measure the residual concentration of the metal ions left in the solution after adsorption onto the RH or CC. Nine sets of blank samples were also prepared. The blanks that were prepared are as follows: bottles with adsorbent and no metal ions; no adsorbent and no metal ions and no adsorbent but with metal ions. The pH values of the blanks were adjusted to 2, 7 and 12 to study the pH variation over 24 hours. All the sets were carried out in duplicate to avoid any discrepancy in experimental results.

Table 2.2. Batch Adsorption Experiments.

Bottle No	pH	Mass of adsorbent (g)	Volume of 0.05 M $NaNO_3$ (ml)	Volume of 5866.67 mg/L of stock solution added (μL)
1	2	3.67	110	375
2	3	3.67	110	375
3	4	3.67	110	375
4	5	3.67	110	375
5	6	3.67	110	375
6	7	3.67	110	375
7	8	3.67	110	375
8	9	3.67	110	375
9	10	3.67	110	375
10	11	3.67	110	375
11	12	3.67	110	375
Blank 1	2	3.67	110	0
	7	3.67	110	0
	12	3.67	110	0
Blank 2	2	0.00	110	375
	7	0.00	110	375
	12	0.00	110	375
Blank 3	2	0.00	110	0
	7	0.00	110	0
	12	0.00	110	0

Adsorption studies were carried with the two different adsorbents and five different metals at 11 initial pH values for the first run. A second run but, with five initial pH values were also carried out. The blank samples were run in duplicate for the two adsorbents and all five metal ions at 3 intermediate pH values ($2 \times 2 \times 5 \times 3 = 60$ samples).

The adsorption behavior of the adsorbent samples was studied by evaluating the percentage removal of the metal ions from the solution using Equation 1:

$$\text{Removal efficiency (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100 \qquad (1)$$

where, C_0 is the initial concentration of the metal ion in the solution (mg/L) which is calculated from the measured concentration of the stock solution and the dilution with the buffer solution and the acid or base solution added to adjust the pH, C_e is the concentration of the metal ion (mg/L) left in the solution after adsorption equilibrium was reached and was measured using the atomic absorption analyzer.

The amount of metal adsorbed onto the adsorbent, q_e (mg/g), was calculated according to the following mass balance equation

$$q_e = \frac{(C_0 - C_e)\,V}{W} \qquad (2)$$

where, C_0 and C_e are the initial and equilibrium concentrations (mg/L) of the metal ion respectively, V is the total volume (L) of the buffer, stock and the acid or base solution and W is the mass of the adsorbent used (g).

2.6. KINETIC STUDIES

It was observed that the final equilibrium pH of the adsorption batch studies were different from the initial pH. Because of this some kinetic studies were run to determine how quickly the pH of the solution changed and whether the metal ion had an effect on the rate of pH change.

For the kinetic studies, a fixed mass of adsorbent was taken in a 125 ml polypropylene bottle and 110 ml of 0.05 M $NaNO_3$ (S/L ratio = 1:30) was added to it and this bottle was spiked with 375 µL with 5866.66 mg/L of the respective metal ion to achieve a nominal concentration of 20 mg/L. There were 10 bottles in total with the two adsorbents and the five different metal ions. The initial pH of each of the bottles was adjusted to a pH value in the range of 7.5 - 9, the pH where the largest drift occurred. These bottles were then kept in the mechanical shaker and pH was recorded after every two hours for 24 hours.

2.7. DESORPTION STUDIES

For any adsorption process, an important factor is the recovery and the regeneration capacity of the adsorbent. Batch desorption studies were performed using the adsorbed metal adsorbent samples that were performed at initial pH of 2. After the adsorption experiments with the various metal ions, the metal-laden adsorbent samples were centrifuged using a Thermo Forma 120 high performance centrifuge by rotating the samples at 7000 rpm for 20 minutes at 23°C. The recovered samples were then washed with deionized water to remove any unadsorbed metals. The metal-laden adsorbent samples were then placed in 125 ml polypropylene bottles and 110 ml of 0.05 M $NaNO_3$

buffer solution was added and the initial pH was adjusted to 2 using 1 M HNO_3. The sealed bottles were then shaken in a mechanical shaker for 24 hrs so that desorption could occur. The bottles were taken from the shaker and the liquid was filtered following the same procedure as in the adsorption experiments and the filtrate was analyzed on the Perkin-Elmer 3110 Atomic Absorption Spectrometer. The same procedure was repeated for each of the different metals and the concentrations of the metals in the aqueous solutions were determined. All the sets were carried out in duplicate to validate the results.

Desorption efficiency was calculated from equation (3):

$$\text{Desorption (\%)} = \frac{q_d}{q_e} \times 100 \tag{3}$$

where, q_d is the mass of the metal ion (mg of metal ion per g of the adsorbent) desorbed and q_e is the mass of the metal ion (mg of metal ion per g of the adsorbent) adsorbed.

The mass of metal ion desorbed, q_d (mg/g) is calculated from the following mass balance equation:

$$q_d = \frac{C_d \times V_d}{W} \tag{4}$$

where, C_d is the concentration of the metal ion (mg/L) left in solution after desorption measured using atomic absorption analyzer, V_d is the total volume (L) of the buffer solution and the acid added to adjust the pH and W is the mass (g) of the metal-laden adsorbent.

3. RESULTS AND DISCUSSION

3.1. CHARACTERIZATION OF ADSORBENTS

Adsorbents are mainly characterized by their surface area and porosity. Table 3.1 summarizes the porous characteristics of rice husk (RH) and coconut coir (CC) obtained from the Autosorb data. The CC has a larger surface area, almost 6 times that of RH. The RH has slightly larger average pore diameter than CC, but has less total specific pore volume. Since the CC has more specific surface area and more specific pore volume, it would be expected that it would have more sorptive capacity if the adsorption was purely a physical adsorption process. For this study, the sorptive capacities of charged metal ions were being studied and the surface charges and surface functional groups play a more significant part in the total sorptive capacity.

Table 3.1. Porous Characteristics of RH and CC.

Adsorbent	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore diameter (nm)
Rice husk	2.48	0.0109	4.903
Coconut coir	16.40	0.0179	4.350

Previous studies has shown the presence of ionizable functional groups such as hydroxyl (-OH) especially the silanol group (Si-OH), carboxyl (-COOH), ketone (-CO), aldehyde (-CHO) and siloxane (Si- O- Si) groups on the surface of RH [60, 61]. The presence of these groups indicates that that RH will have good metal binding capacity and will be an effective adsorbent for removing metal ions [61]. The main functional groups among them involved in the adsorption mechanism of RH are the silanol and the carboxylic groups [62, 63]. The pKa value of carboxylic group is around 4 [64] and that of the silanol group is 7.2 [63].

The CC primarily contains α- cellulose, hemicellulose and lignin [65]. The functional groups in lignin such as the phenolic hydroxyl group (C_6H_5-OH), methoxyl (-OCH_3), carbonyl (-CO) and carboxyl (-COOH) and the hydroxyl (-OH) group in cellulose are the functional groups present on the surface of CC. The main functional groups responsible for the adsorption on the surface of CC are the methoxyl group combined with the aromatic ring and the carbonyl groups [66].

3.2. pH DRIFT METHOD - DETERMINATION OF ZERO POINT OF CHARGE OF ADSORBENTS

The zero point of charge (pH_{ZPC}) of an adsorbent is an important characteristic that determines the pH at which the surface has net electrical neutrality. To determine the zero point of charge of RH and CC, the pH drift method was employed [67, 68, 69]. The pH drift method which was originally developed for activated carbon, provides a quick yet reliable information on the pH_{ZPC} of an adsorbent [70].

During the batch adsorption studies, it was noted that there was a drift in the final equilibrium pH. At low initial pH values there was a slight increase to the final equilibrium pH and at higher initial pH there was a decreasing trend in the final pH. In the pH drift method, the initial pH is plotted against the final equilibrium pH. The pH at the point where the curve cuts the pH $_{\text{initial}}$ = pH $_{\text{final}}$ line is the pH_{ZPC} of the adsorbent [67]. The initial and final equilibrium pH values for each of the batch adsorption studies were plotted and the averages of the pH_{ZPC} values are shown in Table 3.2. Figures 3.1 and 3.2 shows the plot of the final equilibrium pH versus initial pH for Cr (VI) metal ion for RH and CC, respectively. These plots are similar to the plots for the other metal ions. The average values were found to be: pH_{ZPC} for RH = 5.3 and pH_{ZPC} for CC = 4.3. At a pH > pH_{ZPC}, the adsorbent surface will have a negative charge and at a pH < pH_{ZPC}, the adsorbent surface will be positively charged.

Table 3.2. pH_{ZPC} Values for RH and CC Calculated from pH Drift Method.

pHzpc values		**RH**			**CC**	
Metal ions	Run 1	Run 2	Avg.	Run 1	Run 2	Avg.
Cr (VI)	5.3	5.2	5.3	4.3	4.5	4.4
Cr (III)	5.3	5.2	5.3	4.4	4.3	4.4
Cd (II)	5.4	5.4	5.4	4.4	4.4	4.4
Cu (II)	5.4	5.2	5.3	4.4	4.1	4.3
Ni (II)	5.4	5.2	5.3	4.1	4.2	4.2
Average			**5.3**			**4.3**

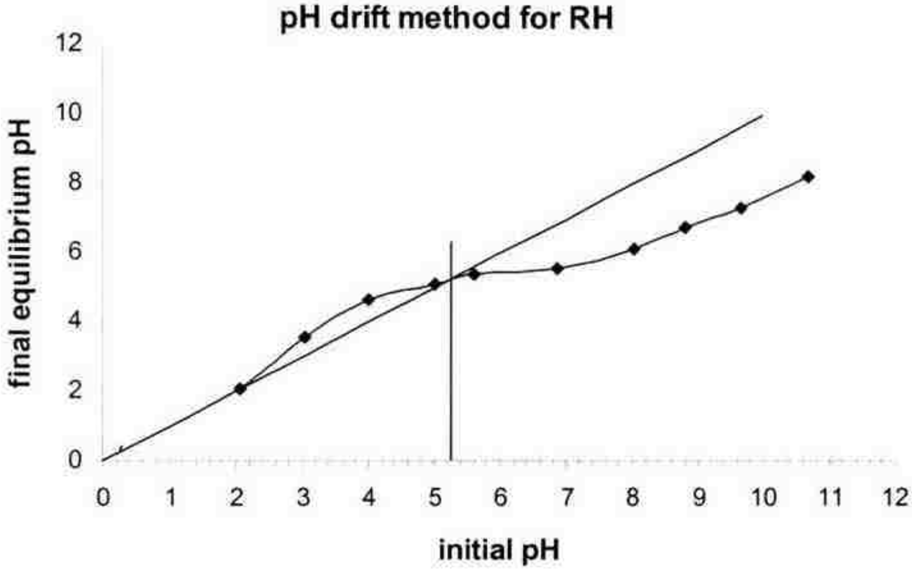

Figure 3.1. Initial pH versus final equilibrium pH for Cr (VI) ion for RH - pH drift method for determining the zero point of charge (pH_{ZPC}).

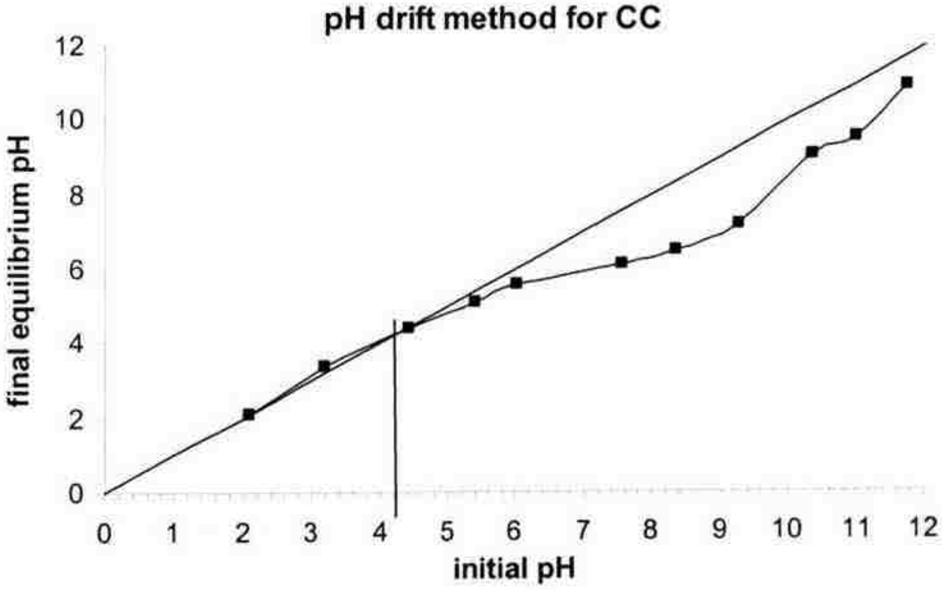

Figure 3.2. Initial pH versus final equilibrium pH for Cr (VI) ion for CC - pH drift method for determining the zero point of charge (pH_{ZPC}).

3.3. BATCH ADSORPTION STUDIES - EFFECT OF pH

pH is a very important parameter in the adsorption process. When the pH of a solution changes, there will be changes in the dissociation of the functional groups on the active sites of the adsorbent which causes a change in the adsorptive process. There will also be changes in the speciation of metals in aqueous solution according to the pH values [71].

The solution pH will have two effects: 1) on the adsorbent, depending on the pH_{ZPC} value the adsorbent will have a net positive or negative charge and 2) on the nature of the metal ion in the solution, i.e., whether it exists in the anionic (-) or cationic (+) state at a given pH.

The pH at which the adsorbent surface has a net neutral charge i.e. when the surface charge density is zero, is called the pH_{ZPC} of the adsorbent. The adsorbent surface can be positively or negatively charged depending on the functional groups present on their surface. The charge on the surface is also dependent on the pH of the solution depending on the net gain or loss of protons (H^+). At a $pH < pH_{ZPC}$, the adsorbent surface will be positively charged and at a $pH > pH_{ZPC}$, the adsorbent surface will be negatively charged. Adsorption onto these adsorbents depends on the nature of the metal ions (cationic or anionic) at the different pH values.

3.3.1. Blank Samples. Blank 1 (adsorbent + buffer solution) showed a drift in the pH value over the equilibrium period, whereas, Blank 2 (metal ion + buffer solution) and Blank 3 (only buffer solution) showed no change in the final equilibrium pH. From these observations we can infer that the change in the final equilibrium pH for the batch adsorption studies is primarily due to the adsorbent.

There was no change in the measured metal ion concentration for Blank 2 which had the metal ion in it over the equilibrium period for the three pH values. This means that there is no effect of the bottle or the buffer solution (0.05 M $NaNO_3$) on the adsorption of metals.

3.3.2. Cr (VI) Adsorption Studies. Figure 3.3 is a plot of the percent removal of Cr (VI) versus the final equilibrium pH on the two adsorbents for both the runs. For RH, the percent removal of Cr (VI) is maximum at pH 3.5 and drops considerably from pH higher than 5. Below a pH value of 3.5 the percent removal drops of to a very low value. The percentage removal is nearly a constant over the pH range of 6 - 12. As shown, the percentage of Cr (VI) removed by CC is a maximum of 94 % at a pH of 3.5 and decreases slightly in the pH range of 4 - 7. At a pH > 7 the percent removal by CC decreases more rapidly and reaches the lowest value of 69 % at a final equilibrium pH of 11.

Figure 3.4 shows the speciation diagram for Cr (VI) ion in aqueous system which was plotted by using the software HYDRA - MEDUSA. The predominant species of Cr (VI) which exists at a pH below 7 is $Cr_2O_7^{2-}$. At a pH value higher than 7, the predominant Cr (VI) species is CrO_4^{2-}. The increased removal of Cr (VI) at lower pH values may be explained by the electrostatic attraction between the adsorbent and the two different adsorbate species in solution at the lower pH

For RH whose pH_{ZPC} is 5.3, at pH values lower than 5.3 the RH surface will be positively charged. The adsorption will be maximum below 5.3 because of the attraction between the anionic species $Cr_2O_7^{2-}$ of Cr (VI) and the positively charged adsorbent surface. At a pH higher than 5.3, the adsorption will decrease because of the electrostatic repulsion between the negatively charged adsorbent surface and the anions of Cr (VI).

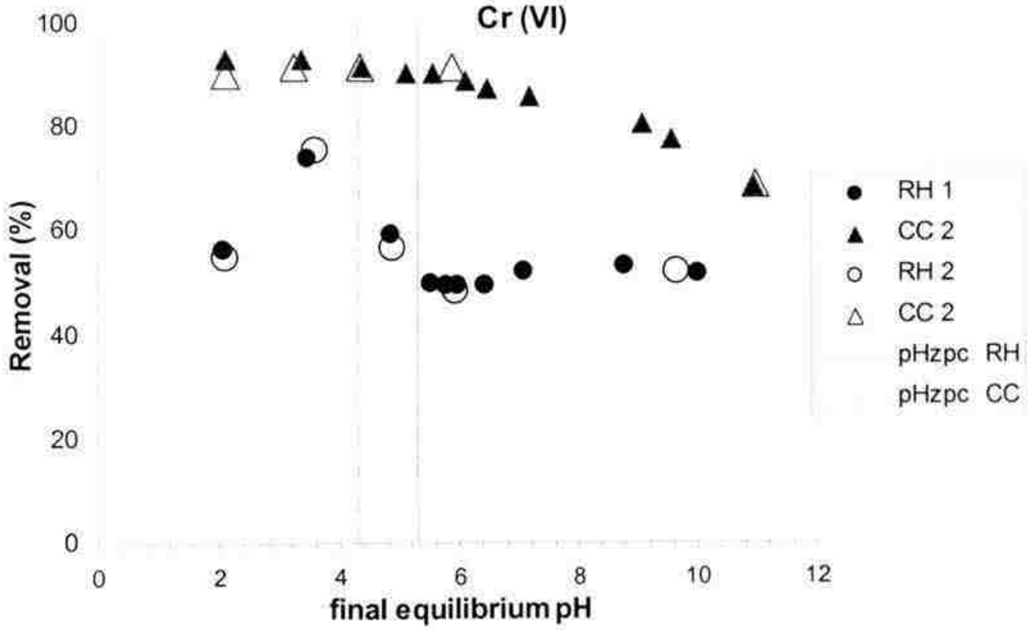

Figure 3.3. Removal efficiency of Cr (VI) ions by RH and CC versus the final equilibrium pH. Agitation time: 24 hrs; S/L ratio: 1:30; initial nominal metal ion concentration: 20mg/L; temperature: 23°C.

In the case of CC whose pH_{ZPC} value is determined to be 4.3, at a $pH < 4.3$, the surface of the CC will be protonated, i.e., its surface will be positively charged. Electrostatic attraction occurs between the positively charged CC surface and the negatively charged $Cr_2O_7^{2-}$ ions. At higher pH values, the observed decrease in adsorption is caused by the competition of the CrO_4^{2-}, the anionic Cr (VI) species at higher pH and the OH^- ions in the solution. Thus, the electrostatic force is an explanation for the increased adsorption of Cr (VI) at lower pH values and decrease in adsorption at higher pH values.

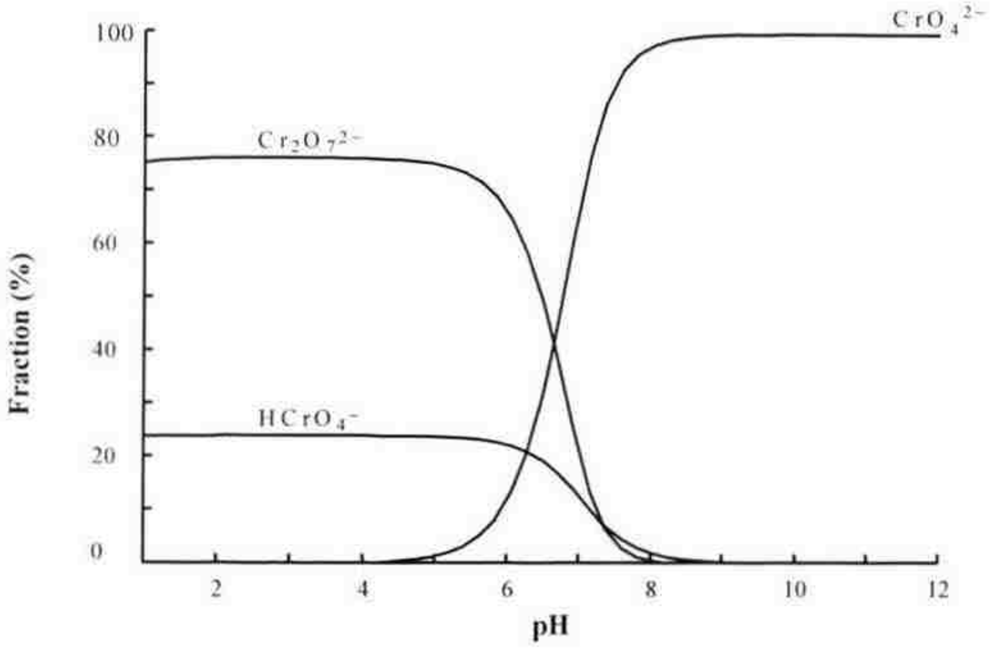

Figure 3.4. Speciation diagram of Cr (VI): Fraction (%) of Cr (VI) versus pH: metal ion concentration: 20 mg/L; ionic strength: 0.05 M; temperature: 25°C.

From literature we see that at a lower pH there can be a reduction of Cr (VI) to Cr (III) [72]. In this study, the Cr (III) which may be formed from the reduction of Cr (VI) was not measured independently. The atomic adsorption technique measured the total chromium in the solution regardless of its ionic state (Cr (VI) or Cr (III)). The equation for Cr (VI) reduction is given by Equation (5) [73]:

$$HCrO_4^- + 7H^+ + 3e^- \Leftrightarrow Cr^{3+} + 4H_2O \qquad (5)$$

Chromic ions exist in aqueous solution as $[Cr\ (H_2O)_6]^{3+}$. The reduction of Cr (VI) to Cr (III) may explain the drop off in adsorption on the CC at a low pH. Since the Cr (III) does not adsorb as readily as Cr (VI), there could be less net adsorption at the lowest pH. By the mechanism of ion exchange, these associated water molecules, $[Cr\ (H_2O)_6]^{3+}$, are exchanged with carboxylic and hydroxyl ions on the surface of RH which causes some adsorption.

3.3.3. Cr (III) Adsorption Studies. Figure 3.5 is a plot of the percent removal of Cr (III) versus final equilibrium pH on the two adsorbents. Cr (III) is less adsorbable than Cr (VI).

We see that for RH, the percent removal is maximum at pH 7 where it has a removal efficiency of 56.3 % and decreases considerably at pH lower than 7. At a pH higher than 7 the percent removal decreases slowly. At a pH below 5 the amount adsorbed remains a constant.

For CC, the optimum pH for Cr (III) removal is at pH of 6.4 and the amount adsorbed decreases considerably at pH lower than 5 and reaches a very low value of 19 % compared to the maximum of 50 % at pH 6.4. At higher pH values above 7 the percent removal drops considerably and there is negligible removal at a pH range of 10-12.

Figure 3.6 show the speciation diagram for Cr (III) ion in aqueous solution using HYDRA-MEDUSA software. The predominant species of Cr (III) at a pH less than 4 is Cr^{3+}. In the pH range of 3 - 8 Cr (III) mainly exists in the cationic form of $Cr_3\ (OH)_4^{5+}$. In the pH range of 7 - 11 there is formation of $Cr\ (OH)_3$.

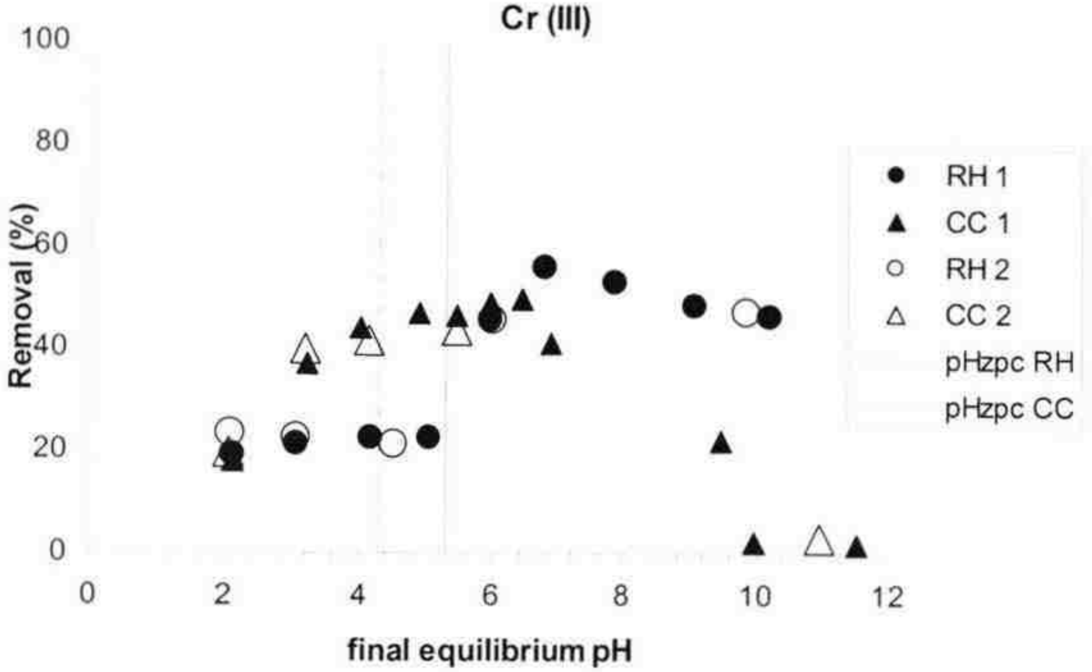

Figure 3.5. Removal efficiency of Cr (III) ions by RH and CC versus the final equilibrium pH. Agitation time: 24 hrs; S/L ratio: 1:30; initial nominal metal ion concentration: 20 mg/L; temperature: 23°C.

The maximum adsorption of Cr (III) at a pH of 6.5 is accounted for by the electrostatic attraction between the negatively charged adsorbent surface (pH > 5.3 for RH and pH > 4.3 for CC) and the cationic species $Cr_3(OH)_4^{5+}$. Similarly, at lower pH values, where the adsorption is observed to be minimum, there occurs electrostatic repulsion between the positively charged adsorbent surface and the cationic species Cr^{3+} which is predominant at lower pH values. The drop in the percent removal of Cr (III) at a pH higher than 6.5 is due to the formation of hydroxide of the Cr (III) [74]. This formation of $Cr(OH)_3$ is evident from the speciation diagram.

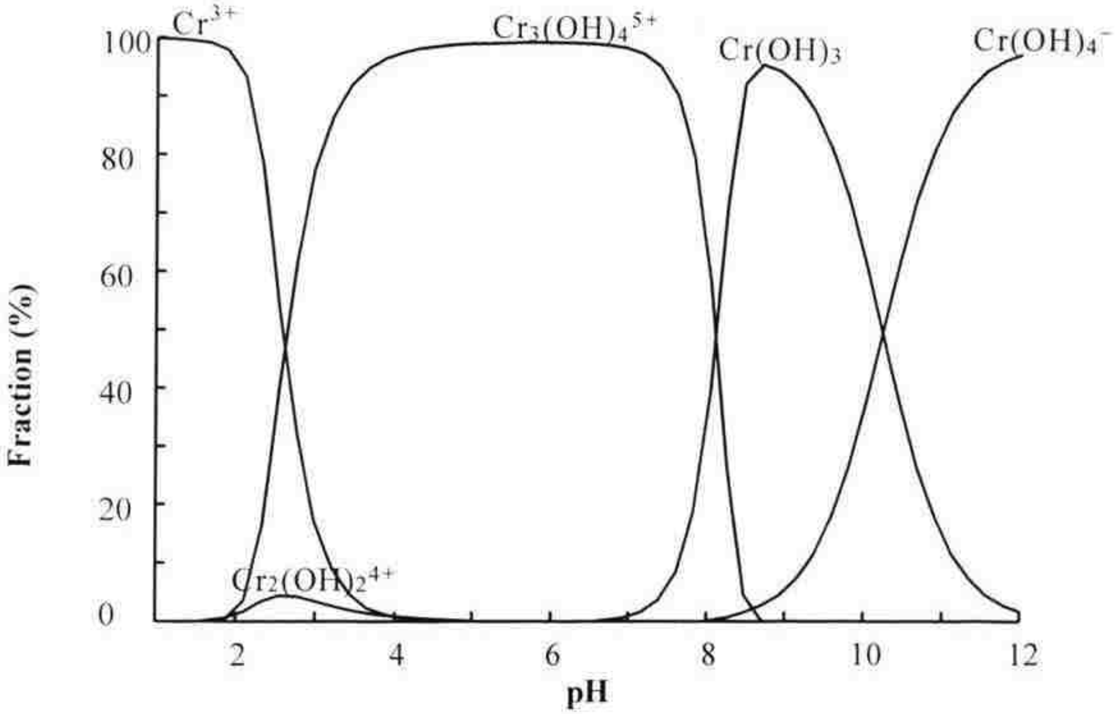

Figure 3.6. Speciation diagram of Cr (III): Fraction (%) of Cr (III) versus pH: metal ion concentration: 20 mg/L; ionic strength: 0.05 M; temperature: 25 °C

The greater adsorption of Cr (III) on RH than on CC can be explained by the presence of the acidic carboxyl (-COOH) group which is predominant on the surface of RH. This mechanism of ion exchange is given by Equation 6 which shows the exchange of ions with the carboxyl functional groups present on RH:

$$2\text{-COOH} + [Cr\,(OH)]^{2+} \Leftrightarrow ([Cr\,(OH)]^{2+} - (COO)_2^{\,-}) + 2H^+ \qquad (6)$$

3.3.4. Cd (II) Adsorption Studies. Figure 3.7 is a plot of percent removal of Cd (II) versus final equilibrium pH on the two adsorbents for both runs. As shown for RH, the adsorption is maximum at pH 5.1 and shows a slight decrease from pH 5.2 to pH 6 and remains a constant in the range of 6 - 10. At pH lower than 5, there is a considerable decrease in the percent removal of Cd (II). It decreases from a 79 % removal at pH 5 to a 55 % at pH 2.

The percent removal of Cd (II) by CC is fairly constant at all pH values and it attains a maximum value at pH 4.5. There is just a slight decrease in percent removal from pH 5 to a pH 10.

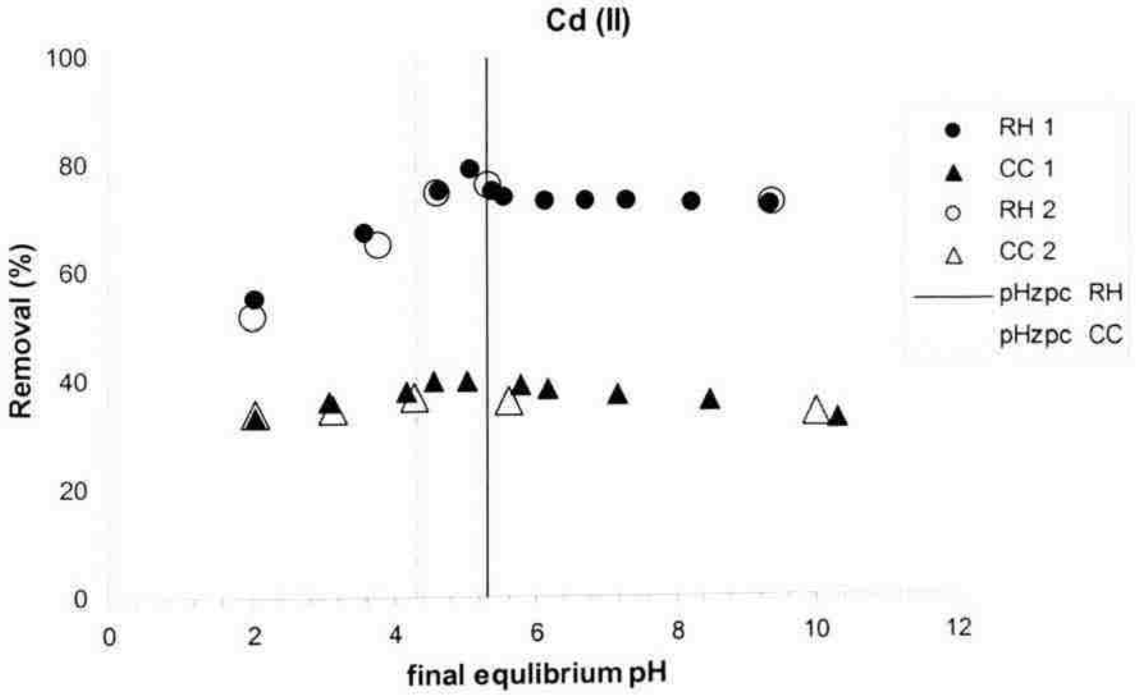

Figure 3.7. Removal efficiency of Cd (II) ions by RH and CC versus the final equilibrium pH. Agitation time: 24 hrs; S/L ratio: 1:30; initial nominal metal ion concentration: 20 mg/L; temperature: 23°C.

Figure 3.8 gives the speciation diagram for Cd (II) which shows the fraction of Cd (II) in the aqueous solution versus pH. This was plotted using the HYDRA-MEDUSA software. As seen from the speciation diagram, the dominant species of Cd (II) at a pH lower than 8 is Cd^{2+}. In the pH range of 9 - 11 Cd (II) mainly exists in the cationic form of $Cd_4(OH)_4^{4+}$ and at pH above 10, Cd (II) is in the form of $Cd(OH)_2$.

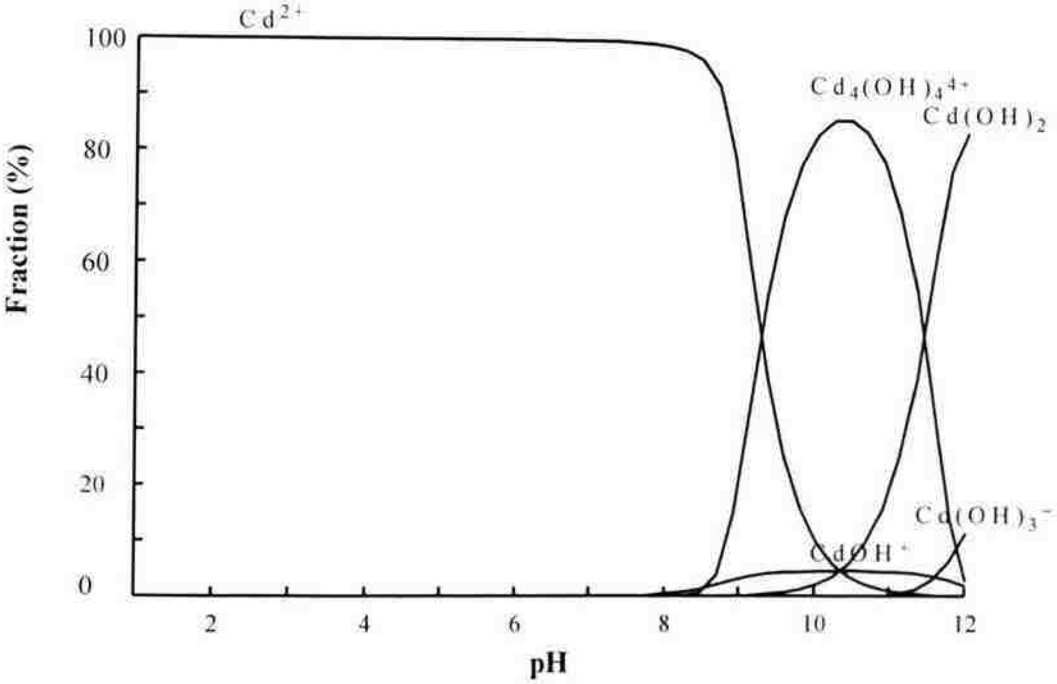

Figure 3.8. Speciation diagram of Cd (II): Fraction (%) of Cd (II) versus pH: metal ion concentration: 20 mg/L; ionic strength: 0.05 M; temperature: 25°C.

The mechanism of adsorption in Cd (II) can be explained by the electrostatic force. The explanation for the increased adsorption capacity for RH at a pH above 4 is that the concentration of H^+ ions decreases with increase in pH, and there will be an increase in the negative surface charges on the adsorbent above the pH_{ZPC} value of 5.3. This difference in surface charges results in the attraction of adsorbing metal cations mainly in the cationic form Cd^{2+} and they more easily get adsorbed onto the adsorbent surface.

In the case of CC, whose surface is negatively charged above a pH > pH_{ZPC} i.e. 4.3, CC should have a maximum adsorption above a pH of 4.3 if the mechanism controlling adsorption is the electrostatic attraction. From the experimental data the maximum adsorption is taking place at a pH 4.5 which confirms that the mechanism of electrostatic force for adsorption.

The Cd (II) adsorption on RH and CC can be also be explained by ion exchange mechanism. The main functional groups on the surface of RH are the carboxyl and hydroxyl groups that have cation exchange property [75] and that on the surface of CC are the phenolic hydroxyl, carbonyl and the methoxyl groups which are responsible for ion exchange onto their surface [76]. The mechanism taking place on RH is shown in Equation 6.

$$2\text{-COOH} + Cd^{2+} \Leftrightarrow \; -((COO^-)_2 - Cd^{2+}) + 2H^+ \qquad (6)$$

3.3.5. Cu (II) Adsorption Studies. Figure 3.9. is a plot of percent removal of Cu(II) versus final equilibrium pH for two sets of experimental run for RH and CC. As shown for RH, the amount adsorbed remains constant at pH values higher than 6. The maximum adsorption is at a pH 8.8 where it has a percent removal of 38.5 %. The percent removal decreases considerably in the pH range 7 - 5 and then remains a constant at pH below 5.

CC has maximum removal of 40 % at a pH of 6.5 and remains almost constant at higher pH values. The amount adsorbed drops slightly at pH lower than 5 and remains almost a constant in the pH range of 2 - 4.

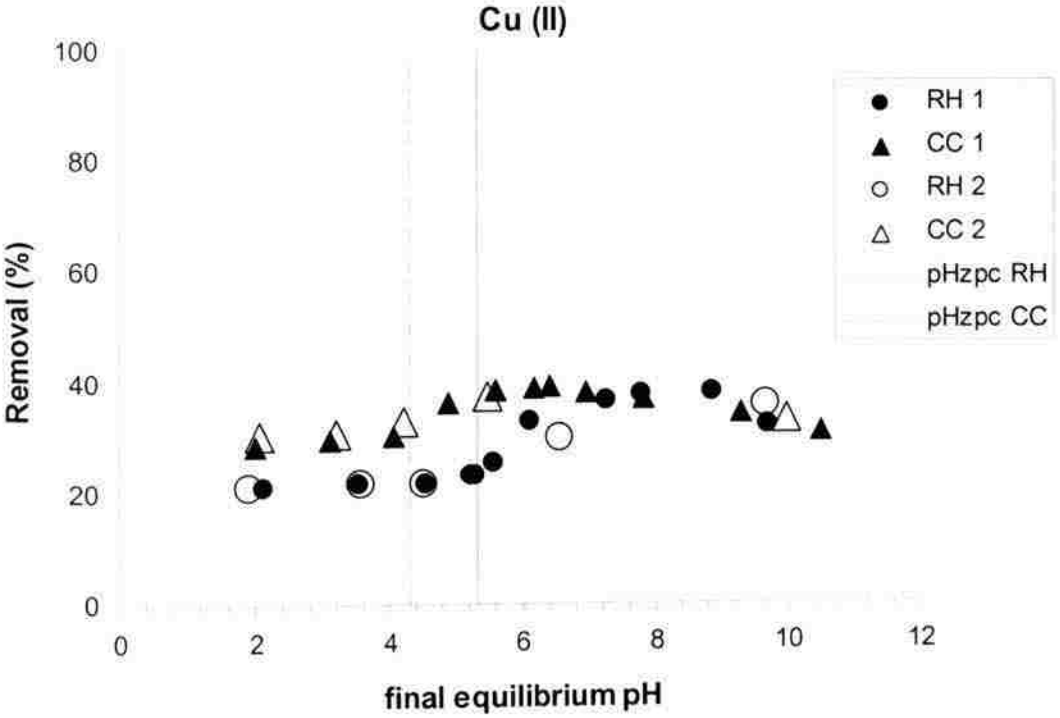

Figure 3.9. Removal efficiency of Cu (II) ions by RH and CC versus the final equilibrium pH. Agitation time: 24 hrs; S/L ratio: 1:30; initial nominal metal ion concentration: 20 mg/L; temperature: 23°C.

Figure 3.10 shows the speciation diagram for Cu (II) ion in aqueous solution which plots the fraction of the species present versus the pH. Cu (II) mainly exists as Cu^{2+} at pH values less than 5. At a higher pH range of 7 - 11 the predominant species of Cu (II) is $Cu_3(OH)_4^{2+}$. At around a pH of 6 there is a very small fraction of $Cu_2(OH)_2^{2+}$ present in the solution.

The relative higher adsorption rate for RH at a pH greater than 6 for RH can be explained by the mechanism of electrostatic force. At a pH > pH $_{ZPC}$ 5.3 for RH, the surface of the adsorbent is negatively charged which leads to an electrostatic attraction between the metal cations ($Cu_2(OH)_2^{2+}$ and $Cu_3(OH)_4^{2+}$) and the adsorbent sites. At a lower pH, the adsorbent surface which is positively charged (pH < 5.3 for RH) and the H^+ ions in the solution inhibit the approach of the metal cations and less adsorption occurs. This justifies that the mechanism involved in the adsorption of Cu (II) is the electrostatic force.

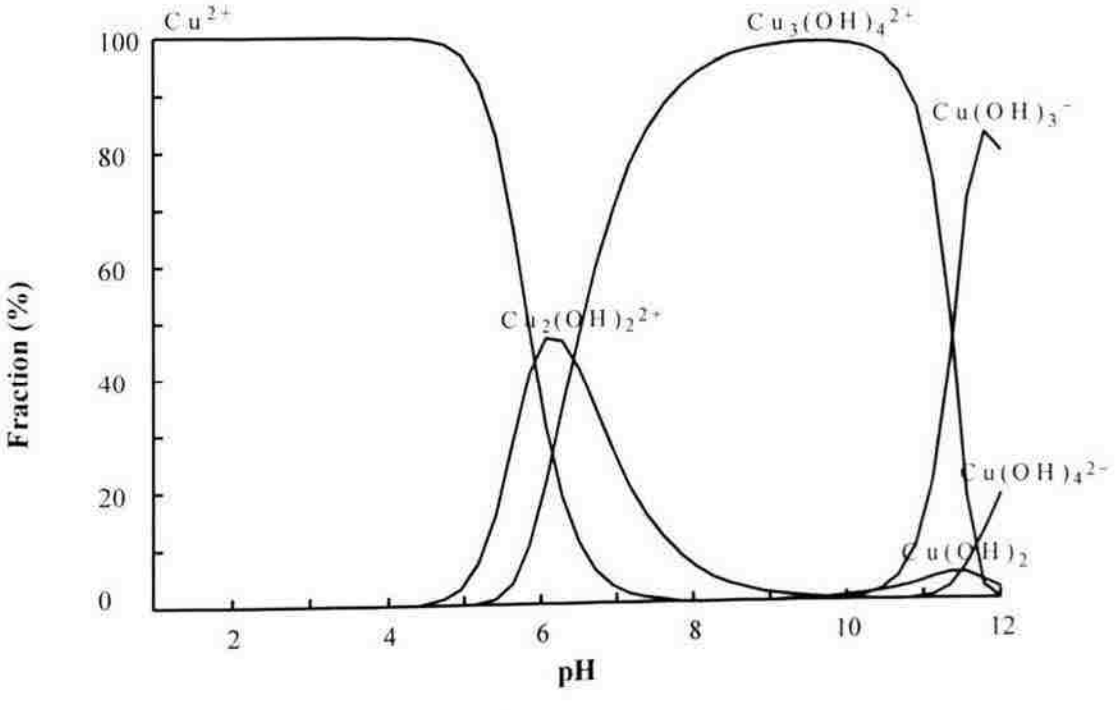

Figure 3.10. Speciation diagram of Cu (II): Fraction (%) of Cu (II) versus pH: metal ion concentration: 20 mg/L; ionic strength: 0.05 M; temperature: 25°C.

From the results we see that CC has greater adsorption at a pH greater than 6. This trend can also be explained by the mechanism of electrostatic force whose surface is negatively charged above a pH of 4.3. The cationic species of Cu (II) gets electrostatically attracted to the negative CC surface above a pH of 4.3.

The acidic carboxylic group on RH is also responsible for adsorption of Cu (II) by ion exchange mechanism which is shown in Equation 7:

$$\text{-COOH} + \text{Cu (OH)}^{+} \Leftrightarrow (\text{-COO}^{-}\text{- Cu (OH)}^{+}) + \text{H}^{+} \tag{7}$$

3.3.6. Ni (II) Adsorption Studies. Figure 3.11 plots the percent removal of Ni (II) versus the final equilibrium pH for two set of experimental runs on the RH and CC.

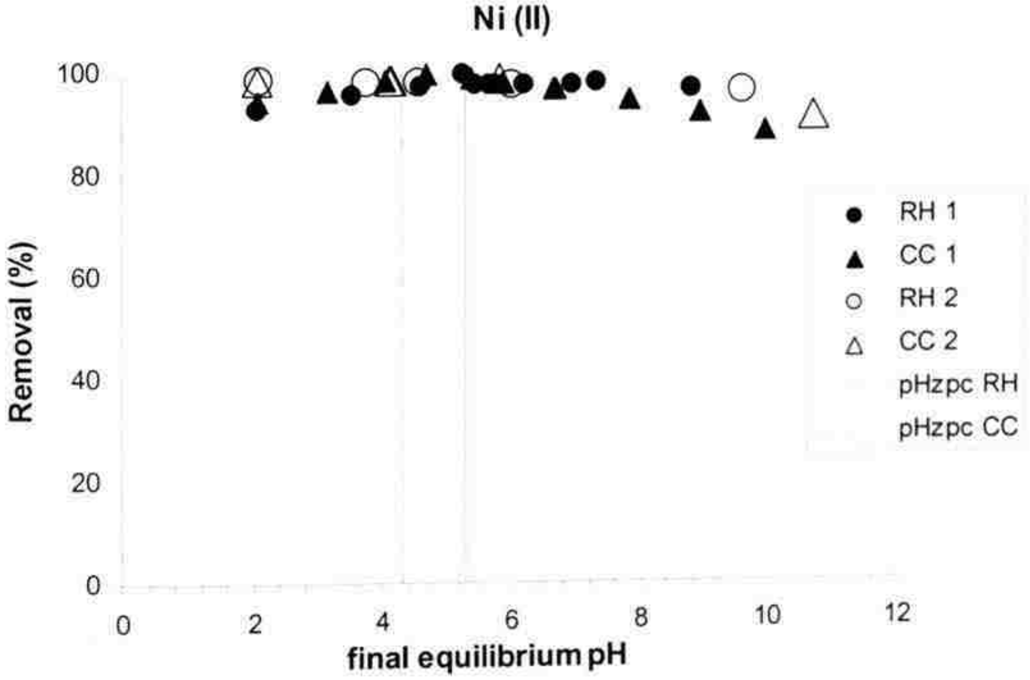

Figure 3.11. Removal efficiency of Ni (II) ions by RH and CC versus the final equilibrium pH. Agitation time: 24 hrs; S/L ratio: 1:30; initial nominal metal ion concentration: 20 mg/L; temperature: 23°C.

A maximum adsorption efficiency of 99.5 % was obtained for Ni (II) using RH at a pH of 5.2. At pH lower than 5 there is a slight decrease in the percent removal of Ni (II). In the pH range of 5.5 - 9 the percent removal almost remained the same.

CC showed a maximum removal of 99.5 % a pH of 4.7. There was a decrease in adsorption above a pH of 6 and it had the lowest removal of 88.0 % at a pH 10. At pH values below 4 there was a slight decrease in the removal efficiency of CC.

Figure 3.12 shows the speciation diagram of Ni (II) ion in the aqueous solution. This plots the fraction of Ni (II) metal ion for various pH values. The speciation diagram was plotted using the software. In the pH range of 2 - 7, Ni (II) exists in the form of Ni^{2+}. In the pH range of 8 - 11, Ni (II) exists as $Ni_4(OH)_4^{4+}$.

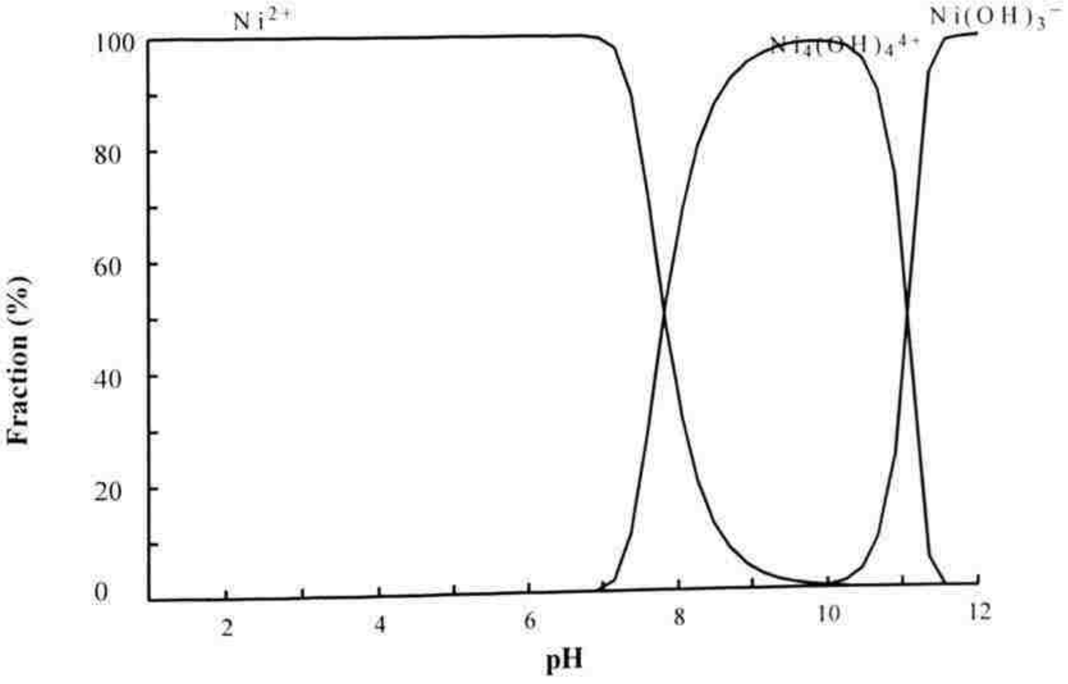

Figure 3.12. Speciation diagram of Ni (II): Fraction (%) of Ni (II) versus pH: metal ion concentration: 20 mg/L; ionic strength: 0.05 M; temperature: 25°C.

At pH > pH_{ZPC} (5.3) for RH and greater than 4.3 for CC, the surface of the adsorbent is negatively charged. At a pH above 7, the cationic species of Ni (II) in solution, as shown in the speciation diagram is a four positive cationic species, $Ni_4(OH)_4^{4+}$ which is greatly attracted to the negatively charged adsorbent surface which explains the high removal efficiency (99.5 %) of both RH and CC at this pH range. In the range above the pH_{ZPC} of the adsorbent and below a pH of 7 there will be maximum electrostatic attraction to the negatively charged adsorbent surface. Similarly, at pH values lower than their pH_{ZPC} which is 5.3 for RH and 4.3 for CC, the adsorbent surface is positively charged and there is electrostatic repulsion between the metal cations (Ni^{2+}) which brings about lesser adsorption.

3.4. COMPARISON OF ADSORBENTS

Figures 3.13 and 3.14 plot the percent removal of each of the metal ions versus the final equilibrium pH. As shown, the maximum adsorption efficiency of RH is in the order of $Ni^{2+} > Cd^{2+} \geq Cr^{6+} \geq Cr^{3+} \geq Cu^{2+}$. The adsorption efficiency of CC is in the order of $Ni^{2+} > Cr^{6+} \geq Cr^{3+} \geq Cd^{2+} \geq Cu^{2+}$.

Comparing the removal efficiency of the two adsorbents RH and CC, we see that CC has higher removal efficiency for Cr (VI), Ni (II) and Cu (II). RH has higher removal efficiency for Cd (II). Both the adsorbents have almost the same efficiency for Cr (III). The higher percent removal of metal ions by CC can be accounted for by the higher surface area of CC which is almost 6 times that of RH as seen from the BET surface area analysis data.

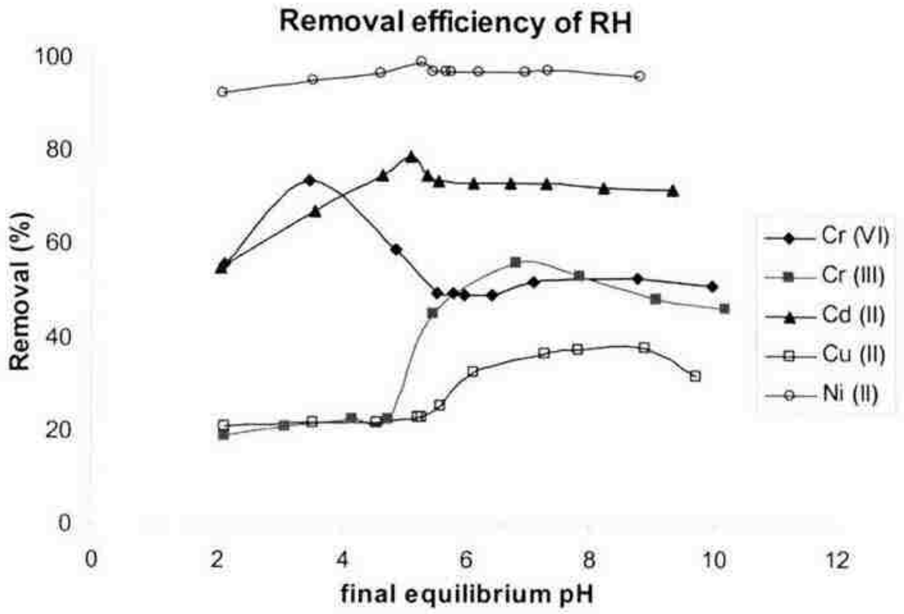

Figure 3.13. Removal efficiency of different metal ions versus final equilibrium pH on RH. Agitation time: 24 hrs; S/L ratio: 1:30; initial metal ion concentration: 20mg/L; temperature: 23°C.

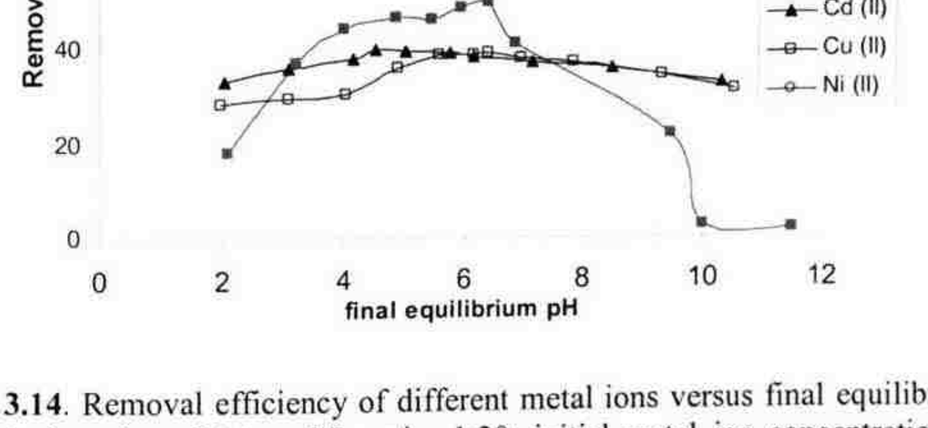

Figure 3.14. Removal efficiency of different metal ions versus final equilibrium pH on CC. Agitation time: 24 hrs; S/L ratio: 1:30; initial metal ion concentration: 20mg/L; temperature: 23°C.

3.5. KINETIC STUDIES

From the batch adsorption data we observed that there was a drift from the initial pH to the final equilibrium pH. At lower initial pH values there was an increase in the final pH and at higher values there was a decrease in the final equilibrium pH. To see how fast the initial pH was changing we ran kinetic studies and the observations are tabulated in Table 3.3. which shows the change in pH of the different metal ion solutions for both RH and CC and their respective initial pH values. The boxes which are left blank are due to procedural error in which the true pH value was not recorded.

Table 3.3. Change in Final pH of the Metal Ion Solution for the Batch Adsorption Studies.

	Δ pH Rice Husk					**Δ pH Coconut coir**				
initial pH	**Cr (VI)**	**Cr (III)**	**Cd**	**Cu**	**Ni**	**Cr (VI)**	**Cr III**	**Cd**	**Cu**	**Ni**
2	-0.02	0.02	0	0.03	0.04	0	0	0.06	0	0
3	0.43	0.16	0.54	0.57	0.53	0.17	-0.02	0.18	0.1	0.04
4	0.69	0.01	0.64	0.54	0.55	-0.06	-0.07	0.08	0.05	-0.05
5	-0.48	-0.17	0.08	0.21	0.25	-0.29	-0.19	-0.13	-0.26	-0.33
6	-1.65	-1.52	-0.22	-0.73	-0.54	-0.44	-0.48	-1.06	-1.20	-0.54
7	-2.01	-2.86	-1.32	-1.36	-1.33	-1.45	-0.68	-1.28	-1.46	-1.35
8	-2.92	-3.05	-1.90	-2.02	-2.20	-1.87	-1.39	-2.18	-1.8	-2.07
9	-3.16	-2.43	-2.07	-1.98	-1.94	-2.11	-1.34	-2.67	-2.15	-2.47
10	-2.32	-1.69	-2.35	-2.07	-2.3	-1.28	-1.03	-1.89	-1.73	-2.22
11	-1.96	-	-2.44	-2.28	-2.77	-1.41	-1.26	-1.37	-1.46	-1.91
12	-	-	-2.25	-1.75	-2.57	-0.81	-0.37	-	-1.14	-1.48

At low pH there was some slight shift to a higher equilibrium pH for some of the ion solutions. For RH, all metal ions had a positive shift at low pH values with Cr (VI) having the largest positive shift in pH. Cd (II), Ni (II) and Cu (II) all had increases in pH for adsorption batches with initial pH up to 5.

For CC, the largest positive shift was for Cd (II) and there were positive shifts for initial pH up to pH 4. For CC only the Cr (III) solution showed no increase in pH.

All of the metal ion solutions demonstrated a decrease in equilibrium pH on both adsorbents for initial pH above 6. Cr (III) and Cr (VI) had the largest decrease in pH on the RH adsorbent. Cd (II) and Ni (II) had the largest decrease in pH on CC. For both adsorbents the greatest change in pH occurred in the 8-9 pH range.

Figures 3.15 and 3.16 show plot of the change in pH from initial to equilibrium for all metal ion adsorption studies versus initial pH for each adsorbent, respectively.

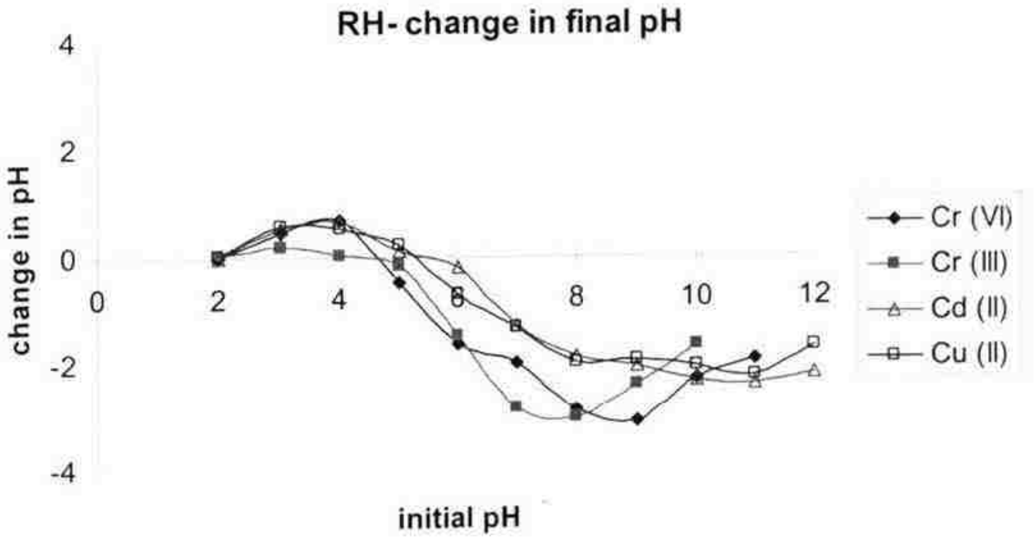

Figure 3.15. Change in pH (Initial - Equilibrium) versus initial pH for each metal ion solution adsorbed on RH. Equilibrium time: 24 hrs and adsorption temperature: 23°C.

Although there is some variation between the different metal ion solutions, the general trends are the same and would indicate that the underlying cause of the change in pH over time is due to the interaction with the adsorbents which may be due to the release of protons from the adsorbents and not due to an interaction with the various forms of the ionic species.

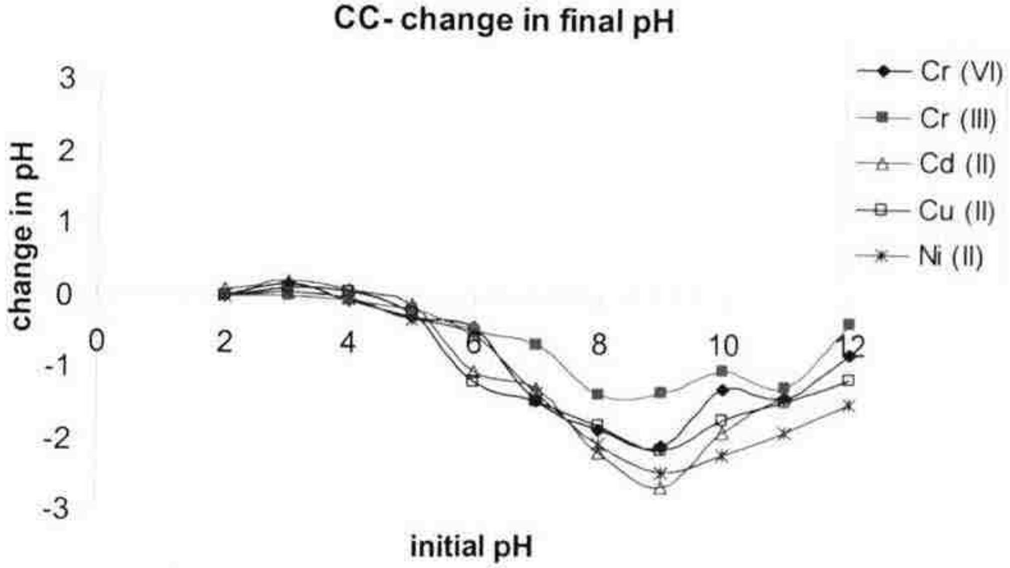

Figure 3.16. Change in pH (Initial - Equilibrium) versus initial pH for each metal ion solution adsorbed on CC. Equilibrium time: 24 hrs and adsorption temperature: 23°C.

Since the pH of the solution should affect the amount adsorbed there was some concern about how quickly the pH was changing. To ensure that the equilibrium was truly at an equilibrium pH and hence equilibrium in terms of adsorption, a kinetic study was run for each metal ion on both adsorbents with the initial pH in the range of 8 - 9 where the greatest change was noted in the adsorption studies. The results are shown in Figures 3.17 and 3.18 which clearly demonstrates that within 3 hours the pH had almost stabilized and the solution was at a constant pH for additional 21 hours for the adsorption to reach equilibrium.

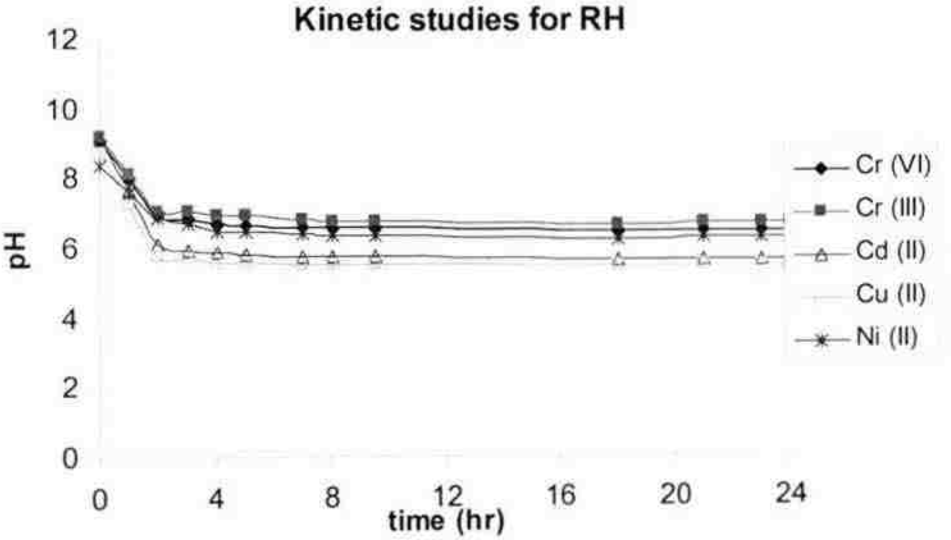

Figure 3.17. Change in pH with time for RH for different metal ions. Time: 24 hrs, temperature: 23^{0}C

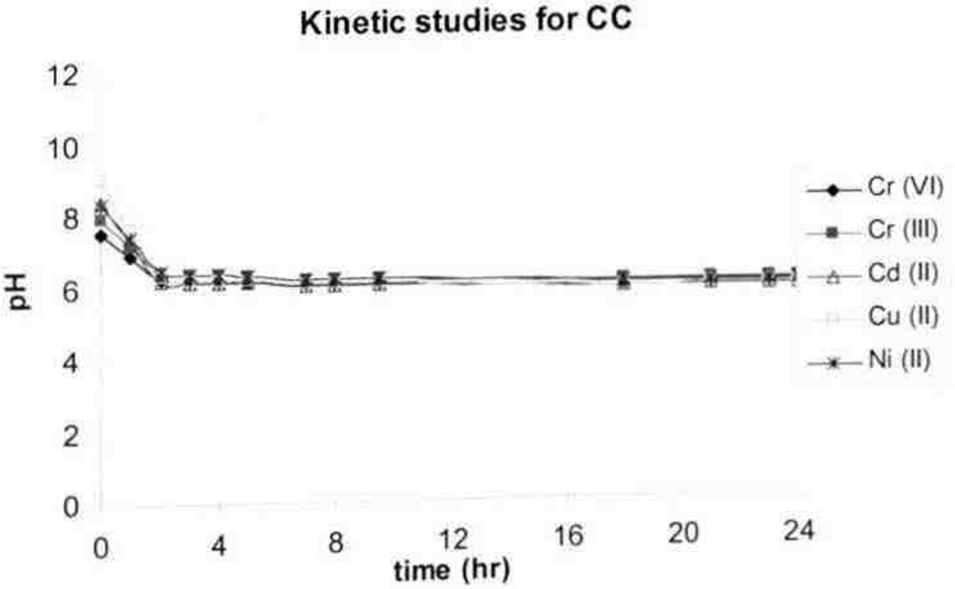

Figure 3.18. Change in pH with time for CC for different metal ions. Time: 24 hr and temperature: 23^{0}C.

3.6. DESORPTION STUDIES

Desorption experiments were conducted on the adsorbents to study their reusability. Figure 3.19 plot desorption efficiencies of the five different metal ions for RH and CC at pH 2. As shown, RH has the highest percent desorption for Cr (III) followed by Cd (II) and Cu (II). The percent desorption of Cr (VI) and Ni (II) on RH is very low. CC has a high percent desorption for Cr (III), Cu (II) and Cd (II) ions in that order. CC has a low percent desorption for Ni (II) and Cr (VI).

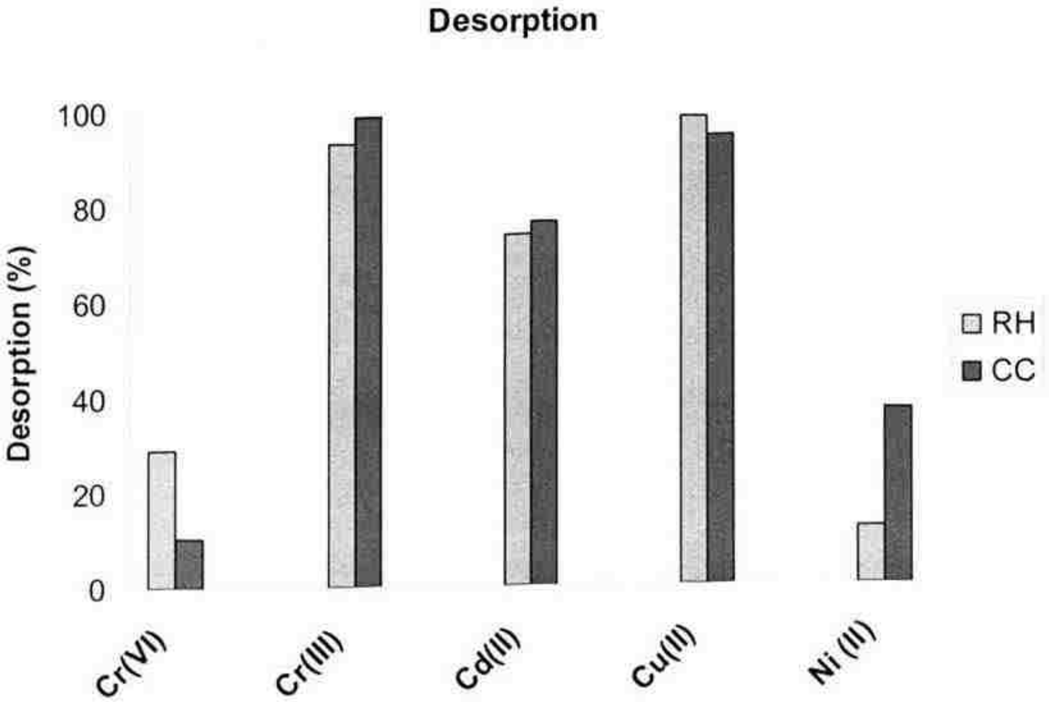

Figure 3.19. Desorption efficiencies of Cr (VI), Cr (III), Cd (II), Cu (II) and Ni (II) for RH and CC initially adsorbed at pH 2 and desorbed at pH 2.

The percent desorption rates of the metal ions from the adsorbents gives us an idea about the nature of adsorption that is happening on the surface of RH and CC. Comparison of Figure 3.19 to Figures 3.13 and 3.14 shows that Cr (VI) and Ni (II) have very low desorption rates for both the adsorbents at pH 2 compared to their high percentage removal at the same pH. This means that the type of adsorption occurring here is chemical adsorption where the adsorbates are more strongly chemically bonded to the adsorbent surface.

Whereas, Cd (II), Cr (III) and Cu (II) have very high desorption rates obtained with an acid solution (pH 2), which indicates that the type of adsorption here is physical adsorption where the metals are not chemically bonded to the adsorbent surface and can easily be desorbed.

4. CONCLUSIONS

The conclusions that can be drawn from the batch adsorption experiments conducted are:

- The adsorption is pH dependent.
- The zero point of charge (pH_{ZPC}) of RH is 5.3 and that of CC is 4.3.
- The mechanisms involved in the adsorption of the metal ions investigated are electrostatic force and ion exchange mechanisms.
- RH has a better efficiency for Cr (VI), Ni (II) and Cd (II) where the highest removals are 99.5% for Ni (II), 80.0% for Cd (II) and 74.0 % for Cr (VI).
- CC removes Cr (VI) and Ni (II) more efficiently than Cd (II), Cr (III) and Cu (II). The highest percentage removals are 93.0 % for Cr (VI) and 99.5 % for Ni (II).
- Comparing the two adsorbents the percentage removal for CC is higher than RH which maybe due to the higher surface area of CC.
- The blank studies show that the change in final equilibrium pH during the batch experiments is due to the adsorbents.
- The kinetic study shows that the drift in pH occurs within the first 3 hours.
- Desorption studies show that RH and CC can be regenerated for reuse for the adsorbates Cr (III), Cu (II) and Cd (II).

From the above conclusions, we see that the adsorbents we studied, RH and CC have potential for being good metal ion sorbents for electroplating wastewater and are good alternatives, especially in developing countries since they are efficient, cheap and easily available.

5. RECOMMENDATIONS

More experiments need to be conducted varying other factors such as the adsorbent dosage, agitation time, sorbate concentration and temperature which have an effect on the adsorption capacity so that optimum parameters to achieve maximum efficiency can be suggested for RH and CC.

APPENDIX A

BATCH ADSORPTION DATA - RUN 1

Table A. 1. Batch adsorption data for Cr (VI) on RH for Run 1

Bottle no	Mass of RH (g)	V_1 (mL)	V_2 (mL)	V_3 (mL)	V (mL)	$pH_{initial}$	pH_{final}	Absorbance	Ce (mg/L)	Co (mg/L)	Ce-Co (mg/L)	qe (mg/g)	Removal (%)
1	3.67	0.91	110	0.375	111.29	2.10	2.12	0.031	8.65	19.77	11.12	0.34	56.25
2	3.67	0.26	110	0.375	110.64	3.03	3.46	0.018	5.14	19.89	14.75	0.44	74.18
3	3.67	0.04	110	0.375	110.42	4.15	4.84	0.029	8.11	19.92	11.82	0.36	59.31
4	3.67	0.02	110	0.375	110.40	6.01	5.53	0.036	10.00	19.93	9.93	0.30	49.82
5	3.67	0.06	110	0.375	110.44	7.44	5.79	0.036	10.00	19.92	9.92	0.30	49.80
6	3.67	0.12	110	0.375	110.50	7.99	5.98	0.036	10.00	19.91	9.91	0.30	49.77
7	3.67	0.2	110	0.375	110.58	9.35	6.43	0.036	10.00	19.90	9.90	0.30	49.74
8	3.67	0.3	110	0.375	110.68	10.24	7.08	0.034	9.46	19.88	10.42	0.31	52.41
9	3.67	1.15	110	0.375	111.53	11.10	8.78	0.033	9.19	19.73	10.54	0.32	53.42
10	3.67	4.98	110	0.375	115.36	11.95	9.99	0.033	9.19	19.07	9.88	0.31	51.82
Blank 1	3.67	0.91	110	0.000	110.91	2.10	2.20	0.000	-	-	-	-	-
	3.67	0.05	110	0.000	110.05	7.02	5.89	0.000	-	-	-	-	-
	3.67	4.95	110	0.000	114.95	11.78	9.95	0.000	-	-	-	-	-
Blank 2	0.00	0.95	110	0.375	111.33	2.07	2.07	0.072	19.73	19.76	-	-	-
	0.00	0.02	110	0.375	110.40	6.98	6.98	0.072	19.73	19.93	-	-	-
	0.00	0.5	110	0.375	110.88	11.56	11.56	0.072	19.73	19.84	-	-	-
Blank 3	0.00	1	110	0.000	111.00	2.01	2.01	0.000	-	-	-	-	-
	0.00	0.03	110	0.000	110.03	7.04	7.04	0.000	-	-	-	-	-
	0.00	0.7	110	0.000	110.70	11.79	11.79	0.000	-	-	-	-	-

V_1 = Volume of NaOH / HNO_3 added

V_2 = Volume of $NaNO_3$ added

V_3 = Volume of 5866.67 mg/ L of Cr (VI) stock solution added

V = Total volume

$pH_{initial}$ = initial pH

pH_{final} = final equilibrium pH

Table A. 2. Batch adsorption data for Cr (VI) on CC for Run 1

Bottle No	Mass ofCC(g)	V_1 (mL)	V_2 (mL)	V_3 (mL)	V (mL)	$pH_{initial}$	pH_{final}	Absorbance	Ce (mg/L)	Co (mg/L)	Co-Ce (mg/L)	qe (mg/g)	Removal (%)
1	3.67	2.60	110	0.375	112.98	2.09	2.09	0.004	1.35	19.47	18.12	0.56	93.06
2	3.67	0.90	110	0.375	111.28	3.19	3.36	0.004	1.35	19.77	18.42	0.56	93.16
3	3.67	0.20	110	0.375	110.58	4.43	4.37	0.005	1.62	19.90	18.27	0.55	91.85
4	3.67	0.50	110	0.375	110.88	5.39	5.10	0.006	1.89	19.84	17.95	0.54	90.47
5	3.67	1.10	110	0.375	111.48	6.00	5.56	0.006	1.89	19.74	17.84	0.54	90.41
6	3.67	1.80	110	0.375	112.18	7.54	6.09	0.007	2.16	19.61	17.45	0.53	88.98
7	3.67	2.30	110	0.375	112.68	8.33	6.46	0.008	2.43	19.53	17.09	0.52	87.54
8	3.67	3.50	110	0.375	113.88	9.27	7.16	0.009	2.70	19.32	16.62	0.52	86.01
9	3.67	9.00	110	0.375	119.38	10.34	9.06	0.012	3.51	18.43	14.92	0.49	80.94
10	3.67	10.00	110	0.375	120.38	10.97	9.56	0.014	4.05	18.28	14.22	0.47	77.82
11	3.67	17.00	110	0.375	127.38	11.73	10.92	0.019	5.41	17.27	11.87	0.41	68.70
Blank 1	3.67	2.70	110	0.000	112.70	2.01	2.02	0.000	-	-	-	-	-
	3.67	1.30	110	0.000	111.30	6.94	6.01	0.000	-	-	-	-	-
	3.67	16.50	110	0.000	126.50	11.69	10.86	0.000	-	--	-	-	-
Blank 2	0.00	0.95	110	0.375	111.33	2.03	2.03	0.072	19.73	19.76	-	-	-
	0.00	0.02	110	0.375	110.40	7.05	7.05	0.072	19.73	19.93	-	-	-
	0.00	0.50	110	0.375	110.88	11.78	11.78	0.072	19.73	19.84	-	-	-
Blank 3	0.00	1.00	110	0.000	111.00	2.04	2.04	0.000	-	-	-	-	-
	0.00	0.03	110	0.000	110.03	6.97	6.97	0.000	-	-	-	-	-
	0.00	0.70	110	0.000	110.70	11.50	11.50	0.000	-	-	--	-	-

V_1 = Volume of NaOH / HNO_3 added

V_2 = Volume of $NaNO_3$ added

V_3 = Volume of 5866.67 mg/ L of Cr (VI) stock solution added

V = Total volume

$pH_{initial}$ = initial pH

pH_{final} = final equilibrium pH

Table A. 3. Batch adsorption data for Cr (III) on RH for Run 1

Bottle no	Mass of RH (g)	V_1 (mL)	V_2 (mL)	V_3 (mL)	V (mL)	$pH_{initial}$	pH_{final}	Absorbance	Ce (mg/L)	Co (mg/L)	Co-Ce (mg/l)	qe (mg/g)	Removal (%)
1	3.67	1.35	110	0.375	111.73	2.09	2.11	0.058	15.95	19.69	3.75	0.11	19.02
2	3.67	0.30	110	0.375	110.68	2.91	3.07	0.057	15.68	19.88	4.20	0.13	21.14
3	3.67	0.05	110	0.375	110.43	4.15	4.16	0.056	15.41	19.92	4.52	0.14	22.68
4	3.67	0.05	110	0.375	110.43	5.03	5.05	0.056	15.41	19.92	4.52	0.14	22.68
5	3.67	0.24	110	0.375	110.62	6.98	5.98	0.039	10.81	19.89	9.08	0.27	45.64
6	3.67	0.70	110	0.375	111.08	9.66	6.80	0.031	8.65	19.81	11.16	0.34	56.33
7	3.67	1.00	110	0.375	111.38	10.90	7.85	0.033	9.19	19.75	10.56	0.32	53.48
8	3.67	2.40	110	0.375	112.78	11.50	9.07	0.036	10.00	19.51	9.51	0.29	48.74
9	3.67	7.20	110	0.375	117.58	11.89	10.20	0.036	10.00	18.71	8.71	0.28	46.56
Blank 1	3.67	1.36	110	0.000	111.36	2.01	2.02	0.000	-	-	-	-	-
	3.67	0.25	110	0.000	110.25	6.97	5.76	0.000	-	-	-	-	-
	3.67	2.40	110	0.000	112.40	11.47	9.67	0.000	-	-	-	-	-
Blank 2	0.00	1.00	110	0.375	111.38	1.98	1.98	0.072	19.73	19.75	-	-	-
	0.00	0.03	110	0.375	110.41	6.93	6.93	0.072	19.73	19.93	-	-	-
	0.00	0.90	110	0.375	111.28	11.73	11.73	0.072	19.73	19.77	-	-	-
Blank 3	0.00	1.00	110	0.000	111.00	2.07	2.07	0.000	-	-	-	-	-
	0.00	0.02	110	0.000	110.02	6.89	6.89	0.000	-	-	-	-	-
	0.00	0.95	110	0.000	110.95	11.67	11.67	0.000	-	-	-	-	-

V_1 = Volume of NaOH / HNO_3 added

V_2 = Volume of $NaNO_3$ added

V_3 = Volume of 5866.67 mg/ L of Cr (III) stock solution added

V = Total volume

$pH_{initial}$ = initial pH

pH_{final} = final equilibrium pH

Table A. 4. Batch adsorption data for Cr (III) on CC for Run 1

Bottle no	Mass of CC (g)	V_1 (mL)	V_2 (mL)	V_3 (mL)	V (mL)	$pH_{initial}$	pH_{final}	Absorbance	Ce (mg/L)	Co (mg/L)	Co-Ce (mg/l)	qe (mg/g)	Removal (%)
1	3.67	2.60	110.00	0.375	112.98	2.11	2.11	0.058	15.95	19.47	3.53	0.11	18.11
2	3.67	0.90	110.00	0.375	111.28	3.19	3.22	0.045	12.43	19.77	7.34	0.22	37.12
3	3.67	0.20	110.00	0.375	110.58	3.99	4.02	0.040	11.08	19.90	8.81	0.27	44.31
4	3.67	0.50	110.00	0.375	110.88	5.07	4.88	0.038	10.54	19.84	9.30	0.28	46.88
5	3.67	1.26	110.00	0.375	111.64	5.94	5.46	0.038	10.54	19.71	9.17	0.28	46.51
6	3.67	1.90	110.00	0.375	112.28	6.64	5.96	0.036	10.00	19.59	9.59	0.29	48.97
7	3.67	2.75	110.00	0.375	113.13	7.82	6.43	0.035	9.73	19.45	9.72	0.30	49.97
8	3.67	3.40	110.00	0.375	113.78	8.22	6.88	0.041	11.35	19.34	7.99	0.25	41.30
9	3.67	9.60	110.00	0.375	119.98	10.49	9.46	0.052	14.32	18.34	4.01	0.13	21.88
10	3.67	12.00	110.00	0.375	122.38	11.24	9.98	0.064	17.57	17.98	0.41	0.01	2.28
11	3.67	21.00	110.00	0.375	131.38	11.89	11.52	0.060	16.49	16.75	0.26	0.01	1.55
Blank 1	3.67	2.80	110	0.000	112.80	2.02	2.03	0.000	-	-	-	-	-
	3.67	2.50	110	0.000	112.50	7.06	5.98	0.000	-	-	-	-	-
	3.67	19.58	110	0.000	129.58	11.75	9.98	0.000	-	-	-	-	-
Blank 2	0.00	1.00	110	0.375	111.38	2.05	2.06	0.072	19.73	19.75	-	-	-
	0.00	0.03	110	0.375	110.41	6.98	6.98	0.072	19.73	19.93	-	-	-
	0.00	0.90	110	0.375	111.28	11.91	11.91	0.072	19.73	19.77	-	-	-
Blank 3	0.00	1.00	110	0.000	111.00	2.09	2.09	0.000	-	-	-	-	-
	0.00	0.02	110	0.000	110.02	6.97	6.97	0.000	-	-	-	-	-
	0.00	0.95	110	0.000	110.95	11.82	11.82	0.000	-	-	-	-	-

V_1 = Volume of NaOH / HNO_3 added

V_2 = Volume of $NaNO_3$ added

V_3 = Volume of 5866.67 mg/ L of Cr (III) stock solution added

V = Total volume

$pH_{initial}$ = initial pH

pH_{final} = final equilibrium pH

Table A. 5. Batch adsorption data for Cd (II) on RH for Run 1

Bottle No	Mass of RH (g)	V_1 (mL)	V_2 (mL)	V_3 (mL)	V (mL)	$pH_{initial}$	pH_{final}	Absorbance	Ce (mg/L)	Co (mg/L)	Co-Ce (mg/l)	qe (mg/g)	Removal (%)
1	3.67	1.36	110	0.375	111.74	2.05	2.05	0.132	8.80	19.69	10.89	0.33	54.47
2	3.67	0.20	110	0.375	110.58	3.03	3.57	0.107	6.48	19.90	13.41	0.40	67.07
3	3.67	0.05	110	0.375	110.43	3.99	4.63	0.090	4.91	19.92	15.02	0.45	75.08
4	3.67	0.00	110	0.375	110.38	5.01	5.09	0.082	4.17	19.93	15.77	0.47	78.83
5	3.67	0.05	110	0.375	110.43	5.60	5.38	0.090	4.91	19.92	15.02	0.45	75.08
6	3.67	0.10	110	0.375	110.48	6.88	5.56	0.093	5.19	19.91	14.73	0.44	73.64
7	3.67	0.20	110	0.375	110.58	8.03	6.13	0.094	5.28	19.90	14.62	0.44	73.09
8	3.67	0.33	110	0.375	110.71	8.80	6.73	0.094	5.28	19.87	14.59	0.44	72.97
9	3.67	0.44	110	0.375	110.82	9.66	7.31	0.094	5.28	19.85	14.58	0.44	72.88
10	3.67	0.97	110	0.375	111.35	10.68	8.24	0.095	5.37	19.76	14.39	0.44	71.94
Blank 1	3.67	1.34	110	0.000	111.34	2.03	2.04	0.000	-	-	-	-	-
	3.67	0.15	110	0.000	110.15	7.08	5.69	0.000	-	-	-	-	-
	3.67	1.01	110	0.000	111.01	11.69	9.87	0.000	-	-	-	-	-
Blank 2	0.00	1.10	110	0.375	111.48	2.05	2.05	0.250	19.72	19.74	-	-	-
	0.00	0.02	110	0.375	110.40	6.98	6.98	0.250	19.72	19.93	-	-	-
	0.00	0.80	110	0.375	111.18	11.56	11.56	0.250	19.72	19.79	-	-	-
Blank 3	0.00	1.15	110	0.000	111.15	2.04	2.04	0.000	-	-	-	-	-
	0.00	0.02	110	0.000	110.02	6.99	6.99	0.000	-	-	-	-	-
	0.00	0.80	110	0.000	110.80	11.78	11.78	0.000	-	-	-	-	-

V_1 = Volume of NaOH / HNO_3 added

V_2 = Volume of $NaNO_3$ added

V_3 = Volume of 5866.67 mg/ L of Cd (II) stock solution added

V = Total volume

$pH_{initial}$ = initial pH

pH_{final} = final equilibrium pH

Table A. 6. Batch adsorption data for Cd (II) on CC for Run 1

Bottle No	Mass of CC (g)	V_1 (mL)	V_2 (mL)	V_3 (mL)	V (mL)	$pH_{initial}$	pH_{final}	Absorbance	Ce (mg/L)	Co (mg/L)	Co-Ce (mg/l)	qe (mg/g)	Removal (%)
1	3.67	2.80	110	0.375	113.175	1.98	2.04	0.177	12.96	19.44	6.48	0.20	33.31
2	3.67	1.00	110	0.375	111.38	2.90	3.08	0.173	12.59	19.75	7.16	0.22	36.25
3	3.67	0.20	110	0.375	110.58	4.08	4.16	0.170	12.31	19.90	7.58	0.23	38.10
4	3.67	0.20	110	0.375	110.58	4.67	4.54	0.166	11.94	19.90	7.95	0.24	39.97
5	3.67	0.45	110	0.375	110.83	6.09	5.03	0.166	11.94	19.85	7.91	0.24	39.83
6	3.67	1.75	110	0.375	112.13	7.06	5.78	0.166	11.94	19.62	7.68	0.23	39.12
7	3.67	2.60	110	0.375	112.98	8.34	6.16	0.166	11.94	19.47	7.53	0.23	38.66
8	3.67	5.00	110	0.375	115.38	9.83	7.16	0.166	11.94	19.07	7.12	0.22	37.36
9	3.67	7.00	110	0.375	117.38	10.37	8.48	0.166	11.94	18.74	6.80	0.22	36.27
10	3.67	14.00	110	0.375	124.38	11.66	10.29	0.165	11.85	17.69	5.84	0.20	33.00
Blank 1	3.67	2.75	110	0.000	112.75	2.04	2.05	0.000	-	-	-	-	-
	3.67	1.75	110	0.000	111.75	7.09	5.80	0.000	-	-	-	-	-
	3.67	13.50	110	0.000	123.50	11.28	9.96	0.000	-	-	-	-	-
Blank 2	0.00	1.10	110	0.375	111.48	2.03	2.03	0.250	19.72	19.74	-	-	-
	0.00	0.02	110	0.375	110.40	7.05	7.05	0.250	19.72	19.93	-	-	-
	0.00	0.80	110	0.375	111.18	11.58	11.58	0.250	19.72	19.79	-	-	-
Blank 3	0.00	1.15	110	0.000	111.15	2.06	2.06	0.000	-	-	-	-	-
	0.00	0.02	110	0.000	110.02	7.03	7.03	0.000	-	-	-	-	-
	0.00	0.80	110	0.000	110.80	11.89	11.89	0.000	-	-	-	-	-

V_1 = Volume of NaOH / HNO_3 added

V_2 = Volume of $NaNO_3$ added

V_3 = Volume of 5866.67 mg/ L of Cd (II) stock solution added

V = Total volume

$pH_{initial}$ = initial pH

pH_{final} = final equilibrium pH

Table A. 7. Batch adsorption data for Cu (II) on RH for Run 1

Bottle No	Mass of RH (g)	V_1 (mL)	V_2 (mL)	V_3 (mL)	V (mL)	$pH_{initial}$	pH_{final}	Absorbance	Ce (mg/L)	Co (mg/L)	Co-Ce (mg/l)	qe (mg/g)	Removal (%)
1	3.67	1.20	110	0.375	111.58	2.08	2.11	0.137	15.55	19.72	4.17	0.13	21.15
2	3.67	0.20	110	0.375	110.58	2.95	3.52	0.137	15.55	19.90	4.35	0.13	21.86
3	3.67	0.05	110	0.375	110.43	4.00	4.54	0.137	15.55	19.92	4.38	0.13	21.97
4	3.67	0.03	110	0.375	110.41	5.01	5.22	0.135	15.31	19.93	4.61	0.14	23.15
5	3.67	0.05	110	0.375	110.43	6.02	5.29	0.135	15.31	19.92	4.61	0.14	23.13
6	3.67	0.10	110	0.375	110.48	6.93	5.57	0.131	14.85	19.91	5.07	0.15	25.44
7	3.67	0.28	110	0.375	110.66	8.14	6.12	0.118	13.34	19.88	6.54	0.20	32.92
8	3.67	0.56	110	0.375	110.94	9.25	7.27	0.111	12.52	19.83	7.31	0.22	36.85
9	3.67	0.80	110	0.375	111.18	9.87	7.80	0.109	12.29	19.79	7.50	0.23	37.89
10	3.67	2.00	110	0.375	112.38	11.16	8.88	0.107	12.06	19.58	7.52	0.23	38.41
11	3.67	4.45	110	0.375	114.83	11.45	9.70	0.115	12.99	19.16	6.17	0.19	32.21
Blank 1	3.67	1.15	110	0.000	111.15	2.02	2.03	0.000	-	-	-	-	-
	3.67	0.09	110	0.000	110.09	6.96	5.58	0.000	-	-	-	-	-
	3.67	5.10	110	0.000	115.10	11.67	9.85	0.000	-	-	-	-	-
Blank 2	0.00	1.10	110	0.375	111.48	2.04	2.04	0.173	19.73	19.74	-	-	-
	0.00	0.03	110	0.375	110.41	7.00	7.00	0.174	19.85	19.93	-	-	-
	0.00	0.95	110	0.375	111.33	11.86	11.86	0.173	19.73	19.76	-	-	-
Blank 3	0.00	1.10	110	0.000	111.10	2.03	2.03	0.000	-	-	-	-	-
	0.00	0.03	110	0.000	110.03	7.06	7.06	0.000	-	-	-	-	-
	0.00	0.95	110	0.000	110.95	11.84	11.84	0.000	-	-	-	-	-

V_1 = Volume of NaOH / HNO_3 added

V_2 = Volume of $NaNO_3$ added

V_3 = Volume of 5866.67 mg/ L of Cu (II) stock solution added

V = Total volume

$pH_{initial}$ = initial pH

pH_{final} = final equilibrium pH

Table A. 8. Batch adsorption data for Cu (II) on CC for Run 1

Bottle No	Mass of CC (g)	V_1 (mL)	V_2 (mL)	V_3 (mL)	V (mL)	$pH_{initial}$	pH_{final}	Absorbance	Ce (mg/L)	Co (mg/L)	Co-Ce (mg/l)	qe (mg/g)	Removal (%)
1	3.67	2.60	110	0.375	112.98	1.98	1.98	0.123	13.92	19.47	5.55	0.17	28.52
2	3.67	0.50	110	0.375	110.88	3.00	3.10	0.123	13.92	19.84	5.92	0.18	29.85
3	3.67	0.20	110	0.375	110.58	4.00	4.05	0.122	13.80	19.90	6.09	0.18	30.63
4	3.67	0.50	110	0.375	110.88	5.15	4.89	0.112	12.64	19.84	7.20	0.22	36.30
5	3.67	1.30	110	0.375	111.68	6.79	5.59	0.107	12.06	19.70	7.64	0.23	38.79
6	3.67	2.00	110	0.375	112.38	7.62	6.16	0.106	11.94	19.58	7.64	0.23	39.00
7	3.67	2.50	110	0.375	112.88	8.22	6.42	0.105	11.83	19.49	7.67	0.24	39.33
8	3.67	3.50	110	0.375	113.88	9.13	6.98	0.106	11.94	19.32	7.38	0.23	38.19
9	3.67	5.00	110	0.375	115.38	9.56	7.83	0.106	11.94	19.07	7.13	0.22	37.37
10	3.67	8.80	110	0.375	119.18	10.77	9.31	0.107	12.06	18.46	6.40	0.21	34.68
11	3.67	15.00	110	0.375	125.38	11.65	10.51	0.107	12.06	17.55	5.49	0.19	31.28
Blank 1	3.67	2.55	110	0.000	112.55	2.00	2.01	0.000	-	-	-	-	-
	3.67	1.40	110	0.000	111.40	6.95	5.68	0.000	-	-	-	-	-
	3.67	15.00	110	0.000	125.00	11.67	10.02	0.000	-	-	-	-	-
Blank 2	0.00	1.10	110	0.375	111.48	2.04	2.04	0.173	19.73	19.74	-	-	-
	0.00	0.03	110	0.375	110.41	6.98	6.98	0.174	19.85	19.93	-	-	-
	0.00	0.95	110	0.375	111.33	11.78	11.78	0.173	19.73	19.76	-	-	-
Blank 3	0.00	1.10	110	0.000	111.10	2.03	2.03	0.000	-	-	-	-	-
	0.00	0.03	110	0.000	110.03	7.07	7.07	0.000	-	-	-	-	-
	0.00	0.95	110	0.000	110.95	11.95	11.95	0.000	-	-	-	-	-

V_1 = Volume of NaOH / HNO_3 added

V_2 = Volume of $NaNO_3$ added

V_3 = Volume of 5866.67 mg/L of Cu (II) stock solution added

V = Total volume

$pH_{initial}$ = initial pH

pH_{final} = final equilibrium pH

Table A. 9. Batch adsorption data for Ni (II) on RH for Run 1

Bottle No	Mass of RH (g)	V_1 (mL)	V_2 (mL)	V_3 (mL)	V (mL)	$pH_{initial}$	pH_{final}	Absorbance	Ce (mg/L)	Co (mg/L)	Co-Ce (mg/l)	qe (mg/g)	Removal (%)
1	3.67	1.34	110	0.375	111.72	2.03	2.07	0.035	1.41	19.69	18.28	0.56	92.82
2	3.67	0.20	110	0.375	110.58	3.00	3.53	0.030	0.91	19.90	18.99	0.57	95.43
3	3.67	0.05	110	0.375	110.43	4.06	4.61	0.027	0.61	19.92	19.32	0.58	96.96
4	3.67	0.00	110	0.375	110.38	5.02	5.27	0.022	0.10	19.93	19.83	0.60	99.49
5	3.67	0.05	110	0.375	110.43	6.00	5.46	0.026	0.51	19.92	19.42	0.58	97.46
6	3.67	0.10	110	0.375	110.48	7.00	5.67	0.026	0.51	19.91	19.41	0.58	97.46
7	3.67	0.13	110	0.375	110.51	7.97	5.77	0.026	0.51	19.91	19.40	0.58	97.46
8	3.67	0.27	110	0.375	110.65	8.15	6.21	0.026	0.51	19.88	19.38	0.58	97.46
9	3.67	0.45	110	0.375	110.83	9.25	6.95	0.026	0.51	19.85	19.35	0.58	97.46
10	3.67	0.55	110	0.375	110.93	10.11	7.34	0.025	0.40	19.83	19.43	0.59	97.96
11	3.67	1.80	110	0.375	112.18	11.39	8.82	0.027	0.61	19.61	19.01	0.58	96.91
Blank 1	3.67	1.36	110	0.000	111.36	2.00	2.02	0.000	-	-	-	-	-
	3.67	0.11	110	0.000	110.11	7.08	5.71	0.000	-	-	-	-	-
	3.67	2.01	110	0.000	112.01	11.89	9.67	0.000	-	-	-	-	-
Blank 2	0.00	0.98	110	0.375	111.36	2.05	2.05	0.216	19.70	19.76	-	-	-
	0.00	0.03	110	0.375	110.41	6.99	6.99	0.218	19.90	19.93	-	-	-
	0.00	0.80	110	0.375	111.18	11.76	11.76	0.216	19.70	19.79	-	-	-
Blank 3	0.00	0.97	110	0.000	110.97	2.04	2.04	0.000	-	-	-	-	-
	0.00	0.03	110	0.000	110.03	7.06	7.06	0.000	-	-	-	-	-
	0.00	0.85	110	0.000	110.85	11.79	11.79	0.000	-	-	-	-	-

V_1 = Volume of NaOH / HNO_3 added

V_2 = Volume of $NaNO_3$ added

V_3 = Volume of 5866.67 mg/ L of Ni (II) stock solution added

V = Total volume

$pH_{initial}$ = initial pH

pH_{final} = final equilibrium pH

Table A. 10. Batch adsorption studies for Ni (II) on CC for Run 1

Bottle No	Mass of CC (g)	V_1 (mL)	V_2 (mL)	V_3 (mL)	V (mL)	$pH_{initial}$	pH_{final}	Absorbance	Ce (mg/L)	Co (mg/L)	Co-Ce (mg/l)	qe (mg/g)	Removal (%)
1	3.67	2.50	110	0.375	112.88	2.07	2.07	0.032	1.11	19.49	18.38	0.57	94.30
2	3.67	0.60	110	0.375	110.98	3.13	3.17	0.028	0.71	19.82	19.12	0.58	96.43
3	3.67	0.25	110	0.375	110.63	4.10	4.05	0.024	0.30	19.89	19.58	0.59	98.48
4	3.67	0.50	110	0.375	110.88	5.02	4.69	0.022	0.10	19.84	19.74	0.60	99.49
5	3.67	1.25	110	0.375	111.63	5.94	5.40	0.023	0.20	19.71	19.51	0.59	98.97
6	3.67	2.10	110	0.375	112.48	7.27	5.92	0.025	0.40	19.56	19.16	0.59	97.93
7	3.67	3.10	110	0.375	113.48	8.78	6.71	0.027	0.61	19.39	18.78	0.58	96.87
8	3.67	3.50	110	0.375	113.88	9.15	6.68	0.027	0.61	19.32	18.71	0.58	96.86
9	3.67	5.60	110	0.375	115.98	10.07	7.85	0.031	1.01	18.97	17.96	0.57	94.68
10	3.67	8.60	110	0.375	118.98	10.85	8.94	0.035	1.41	18.49	17.08	0.55	92.35
11	3.67	12.60	110	0.375	122.98	11.45	9.97	0.041	2.02	17.89	15.87	0.53	88.71
Blank 1	3.67	2.45	110	0.000	112.45	2.02	2.03	0.000	-	-	-	-	-
	3.67	1.45	110	0.000	111.45	6.97	5.98	0.000	-	-	-	-	-
	3.67	12.85	110	0.000	122.85	11.56	9.93	0.000	-	-	-	-	-
Blank 2	0.00	0.98	110	0.375	111.36	2.03	2.03	0.216	19.70	19.76	-	-	-
	0.00	0.03	110	0.375	110.41	7.05	7.05	0.217	19.80	19.93	-	-	-
	0.00	0.80	110	0.375	111.18	11.78	11.78	0.216	19.70	19.79	-	-	-
Blank 3	0.00	0.97	110	0.000	110.97	2.07	2.07	0.000	-	-	-	-	-
	0.00	0.03	110	0.000	110.03	7.04	7.04	0.000	-	-	-	-	-
	0.00	0.85	110	0.000	110.85	11.38	11.38	0.000	-	-	-	-	-

V_1 = Volume of NaOH / HNO_3 added

V_2 = Volume of $NaNO_3$ added

V_3 = Volume of 5866.67 mg/ L of Ni (II) stock solution added

V = Total volume

$pH_{initial}$ = initial pH

pH_{final} = final equilibrium pH

APPENDIX B

BATCH ADSORPTION DATA - RUN 2

Table B. 1. Batch adsorption data of Cr (VI) on RH for Run 2

Bottle no	Mass of RH (g)	V_1 (mL)	V_2 (mL)	V_3 (mL)	V (mL)	$pH_{initial}$	pH_{final}	Absorbance	Ce (mg/L)	Co (mg/L)	Co-Ce (mg/l) 0	qe (mg/g)	Removal (%)
1	3.67	1.30	110	0.375	111.68	2.06	2.10	0.032	8.92	19.70	10.78	0.33	54.73
2	3.67	0.25	110	0.375	110.63	2.85	3.57	0.017	4.86	19.89	15.02	0.45	75.54
3	3.67	0.05	110	0.375	110.43	3.90	4.86	0.031	8.65	19.92	11.27	0.34	56.59
4	3.67	0.07	110	0.375	110.45	7.36	5.95	0.037	10.27	19.92	9.65	0.29	48.44
5	3.67	3.72	110	0.375	114.10	11.77	9.63	0.033	9.19	19.28	10.09	0.31	52.34
Blank 1	3.67	1.45	110	0.000	111.45	1.98	1.99	0.000	-	-	-	-	-
	3.67	0.05	110	0.000	110.05	6.96	5.45	0.000	-	-	-	-	-
	3.67	3.80	110	0.000	113.80	11.68	9.87	0.000	-	-	-	-	-
Blank 2	0.00	1.10	110	0.375	111.48	2.03	2.03	0.072	19.73	19.74	-	-	-
	0.00	0.02	110	0.375	110.40	6.98	6.98	0.072	19.73	19.93	-	-	-
	0.00	0.98	110	0.375	111.36	11.95	11.95	0.072	19.73	19.76	-	-	-
Blank 3	0.00	1.00	110	0.000	111.00	2.04	2.04	0.000	-	-	-	-	-
	0.00	0.04	110	0.000	110.04	6.89	6.89	0.000	-	-	-	-	-
	0.00	1.20	110	0.000	111.20	11.68	11.68	0.000	-	-	-	-	-

V_1 = Volume of NaOH / HNO_3 added

V_2 = Volume of $NaNO_3$ added

V_3 = Volume of 5866.67 mg/ L of Cr (VI) stock solution added

V = Total volume

$pH_{initial}$ = initial pH

pH_{final} = final equilibrium pH

Table B. 2. Batch adsorption data for Cr (VI) on CC for Run 2

Bottle no	Mass of CC (g)	V_1 (mL)	V_2 (mL)	V_3 (mL)	V (mL)	$pH_{initial}$	pH_{final}	Absorbance	Ce (mg/L)	Co (mg/L)	Co-Ce (mg/l)	qe (mg/g)	Removal (%)
1	3.67	2.50	110	0.375	112.88	2.06	2.10	0.006	1.89	19.49	17.60	0.54	90.29
2	3.67	0.90	110	0.375	111.28	3.07	3.23	0.005	1.62	19.77	18.15	0.55	91.80
3	3.67	0.24	110	0.375	110.62	4.17	4.31	0.005	1.62	19.89	18.27	0.55	91.85
4	3.67	1.12	110	0.375	111.50	7.19	5.86	0.005	1.62	19.73	18.11	0.55	91.78
5	3.67	15.00	110	0.375	125.38	11.98	10.96	0.019	5.41	17.55	12.14	0.41	69.20
Blank 1	3.67	2.50	110	0.000	112.50	2.04	2.05	0.000	-	-	-	-	-
	3.67	0.97	110	0.000	110.97	6.97	5.97	0.000	-	-	-	-	-
	3.67	13.50	110	0.000	123.50	11.67	10.45	0.000	-	-	-	-	-
Blank 2	0.00	1.10	110	0.375	111.48	2.06	2.06	0.072	19.73	19.74	-	-	-
	0.00	0.02	110	0.375	110.40	6.87	6.87	0.072	19.73	19.93	-	-	-
	0.00	0.98	110	0.375	111.36	11.58	11.58	0.072	19.73	19.76	-	-	-
Blank 3	0.00	1.00	110	0.000	111.00	2.02	2.02	0.000	-	-	-	-	-
	0.00	0.04	110	0.000	110.04	6.98	6.98	0.000	-	-	-	-	-
	0.00	1.20	110	0.000	111.20	11.86	11.86	0.000	-	-	-	-	-

V_1 Volume of NaOH / HNO_3 added

V_2 Volume of $NaNO_3$ added

V_3 Volume of 5866.67 mg/L of Cr (VI) stock solution added

V Total volume

$pH_{initial}$ initial pH

pH_{final} final equilibrium pH

Table B. 3. Batch adsorption data for Cr (III) on RH for Run 2

Bottle no	Mass of RH (g)	V_1 (mL)	V_2 (mL)	V_3 (mL)	V (mL)	$pH_{initial}$	pH_{final}	Absorbance	Ce (mg/L)	Co (mg/L)	Co-Ce (mg/l)	qe (mg/g)	Removal (%)
1	3.67	1.35	110	0.375	111.73	2.07	2.07	0.055	15.14	19.69	4.56	0.14	23.14
2	3.67	0.30	110	0.375	110.68	2.76	3.06	0.056	15.41	19.88	4.47	0.13	22.50
3	3.67	0.06	110	0.375	110.44	3.68	4.50	0.057	15.68	19.92	4.25	0.13	21.31
4	3.67	0.22	110	0.375	110.60	7.12	6.01	0.039	10.81	19.89	9.08	0.27	45.65
5	3.67	5.00	110	0.375	115.38	11.92	9.84	0.036	10.00	19.07	9.07	0.29	47.56
Blank 1	3.67	1.50	110	0.000	111.50	2.03	2.04	0.000	-	-	-	-	-
	3.67	0.21	110	0.000	110.21	7.00	5.87	0.000	-	-	-	-	-
	3.67	4.95	110	0.000	114.95	11.83	9.79	0.000	-	-	-	-	-
Blank 2	0.00	0.95	110	0.375	111.33	2.03	2.03	0.072	19.73	19.76	-	-	-
	0.00	0.03	110	0.375	110.41	7.02	7.02	0.072	19.73	19.93	-	-	-
	0.00	1.00	110	0.375	111.38	11.65	11.65	0.072	19.73	19.75	-	-	-
Blank 3	0.00	0.95	110	0.000	110.95	2.05	2.05	0.000	-	-	-	-	-
	0.00	0.04	110	0.000	110.04	7.09	7.09	0.000	-	-	-	-	-
	0.00	0.98	110	0.000	110.98	11.71	11.71	0.000	-	-	-	-	-

V_1 = Volume of NaOH / HNO_3 added

V_2 = Volume of $NaNO_3$ added

V_3 = Volume of 5866.67 mg/ L of Cr (III) stock solution added

V = Total volume

$pH_{initial}$ = initial pH

pH_{final} = final equilibrium pH

Table B. 4. Batch adsorption data for Cr (III) on CC for Run 2

Bottle no	Mass of CC(g)	V_1 (mL)	V_2 (mL)	V_3 (mL)	V (mL)	$pH_{initial}$	pH_{final}	Absorbance	Ce (mg/L)	Co (mg/L)	Co-Ce (mg/l)	qe (mg/g)	Removal (%)
1	3.67	2.60	110	0.375	112.98	2.06	2.06	0.057	15.68	19.47	3.80	0.12	19.50
2	3.67	0.90	110	0.375	111.28	3.12	3.20	0.043	11.89	19.77	7.88	0.24	39.85
3	3.67	0.20	110	0.375	110.58	4.17	4.15	0.042	11.62	19.90	8.27	0.25	41.59
4	3.67	1.20	110	0.375	111.58	7.03	5.45	0.040	11.08	19.72	8.64	0.26	43.80
5	3.67	17.00	110	0.375	127.38	11.80	10.95	0.061	16.76	17.27	0.52	0.02	2.98
Blank 1	3.67	2.60	110	0.000	112.60	2.07	2.07	0.000	-	-	-	-	-
	3.67	1.15	110	0.000	111.15	7.05	5.46	0.000	-	-	-	-	-
	3.67	16.00	110	0.000	126.00	11.48	9.74	0.000	-	-	-	-	-
Blank 2	0.00	0.95	110	0.375	111.33	2.06	2.06	0.072	19.73	19.76	-	-	-
	0.00	0.03	110	0.375	110.41	6.98	6.98	0.072	19.73	19.93	-	-	-
	0.00	1.00	110	0.375	111.38	11.92	11.92	0.072	19.73	19.75	-	-	-
Blank 3	0.00	0.95	110	0.000	110.95	2.01	2.01	0.000	-	-	-	-	-
	0.00	0.04	110	0.000	110.04	6.99	6.99	0.000	-	-	-	-	-
	0.00	0.98	110	0.000	110.98	11.89	11.89	0.000	-	-	-	-	-

V_1 = Volume of NaOH / HNO_3 added

V_2 = Volume of $NaNO_3$ added

V_3 = Volume of 5866.67 mg/ L of Cr (III) stock solution added

V = Total volume

$pH_{initial}$ = initial pH

pH_{final} = final equilibrium pH

Table B. 5. Batch adsorption data for Cd (II) on RH for Run 2

Bottle No	Mass of RH (g)	V_1 (mL)	V_2 (mL)	V_3 (mL)	V (mL)	$pH_{initial}$	pH_{final}	Absorbance	Ce (mg/L)	Co (mg/L)	Co-Ce (mg/l)	qe (mg/g)	Removal (%)
1	3.67	1.50	110	0.375	111.88	2.01	2.01	0.139	9.44	19.66	10.22	0.31	51.97
2	3.67	0.15	110	0.375	110.53	3.05	3.77	0.112	6.94	19.91	12.96	0.39	65.11
3	3.67	0.04	110	0.375	110.42	3.88	4.61	0.091	5.00	19.92	14.92	0.45	74.91
4	3.67	0.05	110	0.375	110.43	7.15	6.35	0.088	4.72	19.92	15.20	0.46	76.30
5	3.67	3.00	110	0.375	113.38	11.73	9.37	0.094	5.28	19.40	14.13	0.44	72.80
Blank 1	3.67	1.40	110	0.000	111.40	2.06	2.07	0.000	-	-	-	-	-
	3.67	0.03	110	0.000	110.03	6.94	5.64	0.000	-	-	-	-	-
	3.67	3.00	110	0.000	113.00	11.65	9.32	0.000	-	-	-	-	-
Blank 2	0.00	1.15	110	0.375	111.53	2.04	2.04	0.250	19.72	19.73	-	-	-
	0.00	0.05	110	0.375	110.43	6.98	6.98	0.251	19.81	19.92	-	-	-
	0.00	1.10	110	0.375	111.48	11.86	11.86	0.250	19.72	19.74	-	-	-
Blank 3	0.00	1.10	110	0.000	111.10	2.01	2.01	0.000	-	-	-	-	-
	0.00	0.06	110	0.000	110.06	7.08	7.08	0.000	-	-	-	-	-
	0.00	1.05	110	0.000	111.05	11.96	11.96	0.000	-	-	-	-	-

V_1 = Volume of NaOH / HNO_3 added

V_2 = Volume of $NaNO_3$ added

V_3 = Volume of 5866.67 mg/ L of Cd (II) stock solution added

V = Total volume

$pH_{initial}$ = initial pH

pH_{final} = final equilibrium pH

Table B. 6. Batch adsorption data for Cd (II) on CC for Run 2

Bottle No	Mass of CC (g)	V_1 (mL)	V_2 (mL)	V_3 (mL)	V (mL)	$pH_{initial}$	pH_{final}	Absorbance	Ce (mg/L)	Co (mg/L)	Co-Ce (mg/l)	qe (mg/g)	Removal (%)
1	3.67	2.60	110	0.375	112.98	2.05	2.05	0.176	12.87	19.47	6.60	0.20	33.91
2	3.67	1.00	110	0.375	111.38	2.86	3.13	0.176	12.87	19.75	6.88	0.21	34.84
3	3.67	0.20	110	0.375	110.58	4.15	4.26	0.172	12.50	19.90	7.40	0.22	37.17
4	3.67	1.20	110	0.375	111.58	7.20	5.60	0.173	12.59	19.72	7.13	0.22	36.14
5	3.67	11.20	110	0.375	121.58	11.83	9.99	0.166	11.94	18.10	6.15	0.20	33.99
Blank 1	3.67	2.70	110	0.000	112.70	2.03	2.03	0.000	-	-	-	-	-
	3.67	1.30	110	0.000	111.30	7.11	5.56	0.000	-	-	-	-	-
	3.67	11.00	110	0.000	121.00	11.69	9.78	0.000	-	-	-	-	-
Blank 2	0.00	1.15	110	0.375	111.53	2.01	2.01	0.250	19.72	19.73	-	-	-
	0.00	0.05	110	0.375	110.43	6.95	6.95	0.251	19.81	19.92	-	-	-
	0.00	1.10	110	0.375	111.48	11.68	11.68	0.250	19.72	19.74	-	-	-
Blank 3	0.00	1.10	110	0.000	111.10	2.03	2.03	0.000	-	-	-	-	-
	0.00	0.06	110	0.000	110.06	6.97	6.97	0.000	-	-	-	-	-
	0.00	1.05	110	0.000	111.05	11.47	11.47	0.000	-	-	-	-	-

V_1 = Volume of NaOH / HNO_3 added

V_2 = Volume of $NaNO_3$ added

V_3 = Volume of 5866.67 mg/ L of Cd (II) stock solution added

V = Total volume

$pH_{initial}$ = initial pH

pH_{final} = final equilibrium pH

Table B. 7. Batch adsorption data for Cu (II) on RH for Run 2

Bottle No	Mass of RH (g)	V_1 (mL)	V_2 (mL)	V_3 (mL)	V (mL)	$pH_{initial}$	pH_{final}	Absorbance	Ce (mg/L)	Co (mg/L)	Co-Ce (mg/l) 0	qe (mg/g)	Removal (%)
1	3.67	2.00	110	0.375	112.38	1.91	1.91	0.136	15.43	19.58	4.15	0.13	21.18
2	3.67	0.17	110	0.375	110.55	3.08	3.56	0.137	15.55	19.90	4.35	0.13	21.88
3	3.67	0.04	110	0.375	110.42	3.88	4.52	0.137	15.55	19.92	4.38	0.13	21.97
4	3.67	0.10	110	0.375	110.48	7.85	6.57	0.123	13.92	19.91	6.00	0.18	30.11
5	3.67	3.20	110	0.375	113.58	11.73	9.67	0.110	12.41	19.37	6.96	0.22	35.95
Blank 1	3.67	1.85	110	0.000	111.85	2.05	2.05	0.000	-	-	-	-	-
	3.67	0.25	110	0.000	110.25	7.06	5.85	0.000	-	-	-	-	-
	3.67	3.50	110	0.000	113.50	11.89	10.04	0.000	-	-	-	-	-
Blank 2	0.00	1.10	110	0.375	111.48	2.05	2.05	0.170	19.38	19.74	-	-	-
	0.00	0.05	110	0.375	110.43	6.96	6.96	0.173	19.73	19.92	-	-	-
	0.00	1.00	110	0.375	111.38	11.67	11.67	0.174	19.85	19.75	-	-	-
Blank 3	0.00	1.10	110	0.000	111.10	2.07	2.07	0.000	-	-	-	-	-
	0.00	0.04	110	0.000	110.04	6.98	6.98	0.000	-	-	-	-	-
	0.00	1.00	110	0.000	111.00	11.86	11.86	0.000	-	-	-	-	-

V_1 = Volume of NaOH / HNO_3 added

V_2 = Volume of $NaNO_3$ added

V_3 = Volume of 5866.67 mg/ L of Cu (II) stock solution added

V = Total volume

$pH_{initial}$ = initial pH

pH_{final} = final equilibrium pH

Table B. 8. Batch adsorption data for Cu (II) on CC for Run 2

Bottle No	Mass of CC (g)	V_1 (mL)	V_2 (mL)	V_3 (mL)	V (mL)	$pH_{initial}$	pH_{final}	Absorbance	Ce (mg/L)	Co (mg/L)	Co-Ce (mg/l)	qe (mg/g)	Removal (%)
1	3.67	2.50	110	0.375	112.88	2.07	2.07	0.120	13.57	19.49	5.92	0.18	30.38
2	3.67	0.90	110	0.375	111.28	3.00	3.20	0.121	13.69	19.77	6.08	0.18	30.78
3	3.67	0.21	110	0.375	110.59	4.18	4.20	0.118	13.34	19.89	6.56	0.20	32.96
4	3.67	1.15	110	0.375	111.53	6.88	5.47	0.109	12.29	19.73	7.44	0.23	37.69
5	3.67	11.30	110	0.375	121.68	11.78	9.96	0.107	12.06	18.08	6.02	0.20	33.31
Blank 1	3.67	2.70	110	0.000	112.70	1.99	1.99	0.000	-	-	-	-	-
	3.67	1.25	110	0.000	111.25	7.06	5.89	0.000	-	-	-	-	-
	3.67	10.65	110	0.000	120.65	11.38	9.96	0.000	-	-	-	-	-
Blank 2	0.00	1.10	110	0.375	111.48	2.01	2.01	0.173	19.73	19.74	-	-	-
	0.00	0.05	110	0.375	110.43	6.89	6.89	0.173	19.73	19.92	-	-	-
	0.00	1.00	110	0.375	111.38	11.89	11.89	0.173	19.73	19.75	-	-	-
Blank 3	0.00	1.10	110	0.000	111.10	2.03	2.03	0.000	-	-	-	-	-
	0.00	0.04	110	0.000	110.04	7.03	7.03	0.000	-	-	-	-	-
	0.00	1.00	110	0.000	111.00	11.76	11.76	0.000	-	-	-	-	-

V_1 = Volume of NaOH / HNO_3 added

V_2 = Volume of $NaNO_3$ added

V_3 = Volume of 5866.67 mg/ L of Cu (II) stock solution added

V = Total volume

$pH_{initial}$ = initial pH

pH_{final} = final equilibrium pH

Table B. 9. Batch adsorption data for Ni (II) on RH for Run 2

Bottle No	Mass of RH (g)	V_1 (mL)	V_2 (mL)	V_3 (mL)	V (mL)	$pH_{initial}$	pH_{final}	Absorbance	Ce (mg/L)	Co (mg/L)	Co-Ce (mg/l)	qe (mg/g)	Removal (%)
1	3.67	1.15	110	0.375	111.53	2.08	2.12	0.024	0.30	19.73	19.42	0.59	98.46
2	3.67	0.15	110	0.375	110.53	3.06	3.75	0.025	0.40	19.91	19.50	0.59	97.97
3	3.67	0.05	110	0.375	110.43	3.56	4.56	0.025	0.40	19.92	19.52	0.59	97.97
4	3.67	0.05	110	0.375	110.43	7.24	6.04	0.026	0.51	19.92	19.42	0.58	97.46
5	3.67	3.70	110	0.375	114.08	11.77	9.61	0.028	0.71	19.29	18.58	0.58	96.33
Blank 1	3.67	1.20	110	0.000	111.20	2.01	2.03	0.000	-	-	-	-	-
	3.67	0.10	110	0.000	110.10	7.08	5.79	0.000	-	-	-	-	-
	3.67	3.50	110	0.000	113.50	11.54	9.83	0.000	-	-	-	-	-
Blank 2	0.00	0.99	110	0.375	111.37	2.03	2.03	0.216	19.70	19.75	-	-	-
	0.00	0.05	110	0.375	110.43	6.93	6.93	0.217	19.80	19.92	-	-	-
	0.00	1.10	110	0.375	111.48	11.83	11.83	0.216	19.70	19.74	-	-	-
Blank 3	0.00	1.10	110	0.000	111.10	2.01	2.01	0.000	-	-	-	-	-
	0.00	0.04	110	0.000	110.04	6.98	6.98	0.000	-	-	-	-	-
	0.00	0.99	110	0.000	110.99	11.57	11.57	0.000	-	-	-	-	-

V_1 = Volume of NaOH / HNO_3 added

V_2 = Volume of $NaNO_3$ added

V_3 = Volume of 5866.67 mg/ L of Ni (II) stock solution added

V = Total volume

$pH_{initial}$ = initial pH

pH_{final} = final equilibrium pH

Table B. 10. Batch adsorption data for Ni (II) on CC for Run 2

Bottle No	Mass of CC (g)	V_1 (mL)	V_2 (mL)	V_3 (mL)	V (mL)	$pH_{initial}$	pH_{final}	Absorbance	Ce (mg/L)	Co (mg/L)	Co-Ce (mg/l)	qe (mg/g)	Removal (%)
1	3.67	2.50	110	0.375	112.88	2.04	2.06	0.024	0.30	19.49	19.19	0.59	98.45
2	3.67	0.90	110	0.375	111.28	3.04	4.15	0.024	0.30	19.77	19.47	0.59	98.47
3	3.67	0.25	110	0.375	110.63	4.28	4.13	0.024	0.30	19.89	19.58	0.59	98.48
4	3.67	1.35	110	0.375	111.73	6.92	5.85	0.023	0.20	19.69	19.49	0.59	98.97
5	3.67	15.00	110	0.375	125.38	11.84	10.68	0.036	1.52	17.55	16.03	0.55	91.37
Blank 1	3.67	2.50	110	0.000	112.50	2.05	2.05	0.000	-	-	-	-	-
	3.67	1.40	110	0.000	111.40	7.03	5.89	0.000	-	-	-	-	-
	3.67	13.00	110	0.000	123.00	11.59	10.01	0.000	-	-	-	-	-
Blank 2	0.00	0.99	110	0.375	111.37	2.05	2.05	0.216	19.70	19.75	-	-	-
	0.00	0.05	110	0.375	110.43	6.97	6.97	0.218	19.90	19.92	-	-	-
	0.00	1.10	110	0.375	111.48	11.69	11.69	0.216	19.70	19.74	-	-	-
Blank 3	0.00	1.10	110	0.000	111.10	2.07	2.07	0.000	-	-	-	-	-
	0.00	0.04	110	0.000	110.04	6.98	6.98	0.000	-	-	-	-	-
	0.00	0.99	110	0.000	110.99	11.66	11.66	0.000	-	-	-	-	-

V_1 = Volume of NaOH / HNO_3 added

V_2 = Volume of $NaNO_3$ added

V_3 = Volume of 5866.67 mg/ L of Ni (II) stock solution added

V = Total volume

$pH_{initial}$ = initial pH

pH_{final} = final equilibrium pH

APPENDIX C

DESORPTION STUDIES DATA

Table C.1. Desorption results for RH

Metal ions	**$pH_{in\ itial}$**	**Co -Ce (mg/L)**	**qe (mg/g)**	**$pH_{initial}$**	**V (mL)**	**Absorbance**	**Ce_d (mg/L)**	**qd (mg/g)**	**Recovery (%)**
Cr(VI)	2.10	11.12	0.34	2.00	111.10	0.011	3.24	0.10	29.12
Cr(III)	2.09	3.75	0.11	2.00	111.10	0.012	3.51	0.11	93.29
Cd(II)	2.05	10.89	0.33	2.00	111.10	0.125	8.15	0.25	74.38
Cu(II)	2.08	4.17	0.13	2.00	111.10	0.039	4.15	0.13	99.10
Ni (II)	2.03	18.28	0.56	2.00	111.10	0.043	2.22	0.07	12.09

$pH_{initial}$ - initial pH

V - Volume of 0.05 M $NaNO_3$ + 1 M HNO_3

qe - mass of metal ion adsorbed per gram of adsorbent

Ce_d - Desorption equilibrium concentration

qd - mass of metal ion desorbed per gram of adsorbent

Table C.2. Desorption results for CC

Metal ions	$pH_{initial}$	Co -Ce (mg/L)	qe (mg/g)	$pH_{initial}$	V (mL)	Absorbance	Ce_d (mg/L)	qd (mg/g)	Recovery (%)
Cr(VI)	2.09	18.12	0.56	2.00	112.50	0.006	1.89	0.06	10.40
Cr(III)	2.11	3.53	0.11	2.00	112.50	0.012	3.51	0.11	99.19
Cd	1.98	6.48	0.20	2.00	112.50	0.091	5.00	0.15	76.75
Cu	1.98	5.56	0.17	2.00	112.50	0.049	5.31	0.16	95.26
Ni	2.07	18.38	0.57	2.00	112.50	0.089	6.87	0.21	37.25

$pH_{initial}$ - initial pH

V - Volume of 0.05 M $NaNO_3$ + 1 M HNO_3

qe - mass of metal ion adsorbed per gram of adsorbent

Ce_d - Desorption equilibrium concentration

qd - mass of metal ion desorbed per gram of adsorbent

APPENDIX D

KINETIC STUDY DATA

Table D.1. Kinetic studies data for RH and CC

	pH Rice Husk					pH Coconut coir				
Time(hr)	Cr(VI)	Cr(III)	Cd(II)	Cu(II)	Ni(II)	Cr(VI)	Cr(III)	Cd(II)	Cu(II)	Ni(II)
0	9.11	9.23	9.15	8.75	8.36	7.55	7.92	8.43	9.03	8.37
1	8.04	8.14	7.64	7.27	7.62	6.91	7.17	7.33	7.67	7.42
2	6.97	7.05	6.13	5.79	6.88	6.26	6.42	6.23	6.31	6.47
3	6.82	7.05	5.95	5.68	6.69	6.19	6.36	6.16	6.23	6.36
4	6.72	6.96	5.86	5.59	6.49	6.19	6.36	6.14	6.21	6.35
5	6.67	6.95	5.83	5.58	6.48	6.17	6.32	6.12	6.18	6.32
7	6.61	6.84	5.78	5.55	6.41	6.09	6.23	6.04	6.10	6.21
8	6.59	6.79	5.76	5.53	6.37	6.07	6.21	6.03	6.09	6.20
9.5	6.57	6.78	5.75	5.52	6.35	6.06	6.19	6.01	6.07	6.18
18	6.50	6.68	5.66	5.44	6.26	5.94	6.06	5.90	5.94	6.04
21	6.49	6.69	5.67	5.45	6.27	5.95	6.07	5.91	5.95	6.05
23	6.49	6.69	5.67	5.45	6.27	5.95	6.07	5.91	5.95	6.05
24	6.49	6.69	5.67	5.45	6.27	5.95	6.07	5.91	5.95	6.05

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