INVESTIGATION OF THE ADSORPTION PROCESS OF HEXAVALENT CHROMIUM WITH POLYANILINE / COCONUT COIR COMPOSITE

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DECLARATION

I do hereby declare that the work reported in this project report/thesis was exclusively carried out by me under the supervision of Dr S. S. Gunathilake. It describes the results of my own independent research except where due reference has been made in the text. No part of this project report/thesis has been submitted earlier or concurrently for the same or any other degree.

Date: ……. ……..

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Pollution of drinking water is a pragmatic problem and a great research interest. Out of many causes for water pollution, contamination by heavy metals is considered to be a major source. Chromium and its compounds are released to water bodies from various industries such as electroplating, leather tanning, paint, textile, and steel industries. Hexavalent chromium is identified as carcinogenic, mutagenic and known to cause liver damage, pulmonary congestion and causes skin irritation resulting in ulcer formation. Therefore, it is important to remove chromium from wastewater, before discharging into the environment. Emaraldine Base form of Polyaniline was grown on coconut coir by chemical oxidation polymerization of aniline in the presence coconut coir. In this reporting work, the resultant polyaniline / coconut coir (PANI/CC) composite was tested as an adsorbent and was experimented for adsorption kinetics. Initial studies performed on a mixture of solution containing chromium, copper, nickel, zinc and cadmium with Atomic emission spectroscopy showed that the PANI/CC composite exhibits adsorption capacity of 34% for chromium and 7% for copper, 6 % nickel and 2% > for zinc and cadmium. Since the adsorption capacity is considerably higher for chromium, the condition for chromium adsorption on PANI/CC was optimized. The optimized conditions for adsorption were found to be 5 pH, 60 minutes of shaking time and 60 minutes settling time with a 0.10 g PANI/CC composite dosage. With these conditions maximum adsorption capacity of 75% was observed for hexavalent chromium on PANI/CC composite. XRF analysis further confirmed the adsorption of Cr(VI) on PANI/CC composite. Adsorption data were fitted to Langmuir adsorption isotherm at low concentrations and Freundlich isotherm at higher concentrations. Results reveal multilayer adsorption formation at higher concentrations. Adsorption kinetics fitted more to pseudo second order kinetic model with an R^2 value of 0.96 suggests that the process is chemisorption. Furthermore, desorption studies indicated that it does not harm natural water bodies since desorption governs only at strong acidic conditions (pH<2).

To my Loving

Parents and Teachers

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CHAPTER 1

INTRODUCTION

1.1 Water

1.1.1 Properties of Water

Water is the only substance that exists naturally on earth in all three physical states of matter - gas, liquid and solid. Naturally there is a constant cycling of water among land, oceans and the atmosphere. About 71% of the Earth's surface is water-covered, and the oceans hold about 97% percent of all Earth's water. The rest 3% is found in glaciers, ground water, and in inland water bodies; tanks, ponds, lakes and rivers, out of which 75% is trapped in ice caps and glaciers. Drinking water, when taken together, constitutes less than 0.01% of the total water in the planet [1]. Pure water is a colourless, odourless and tasteless liquid that is essential to all living beings. Further, water is the raw material of glucose, which is the basic molecule of food made by plants through photosynthesis. Without water, life would not be able to survive on the earth. Thus, water is a very important substance which should be protected and should not be polluted.

Water has several unique physical and chemical properties which make it essential for all living beings. These properties can easily be understood by considering the structure of the water molecule, which has a bond angle of 105^0. The polarity, readily availability, ability to be obtained in pure form and convenient liquid range make it an excellent solvent for many ionic compounds and salts. It has become the basic transport medium for nutrients and waste in living beings. Due to hydrogen bonds, water has a high boiling point and a high heat capacity as compared to the other solvents. As the maximum density of water occurs at 4 °C, ice tends to float on water, this is an important phenomenon for the survival of aquatic life.

1.1.2 Pollution of Water

Environmental pollution has become a severe problem in the world nowadays. Pollution can occur in land, air and water, mainly due to anthropogenic activities such as urbanization, industrialization and increase of population. Pollution can be defined as the introduction of a substance which has harmful or poisonous effects, in greater concentrations which exceeds the natural limit. Water is generally referred as polluted when its physical, chemical or biological qualities become harmful to man or aquatic life. Some changes of physical characteristics that are referred to as water pollution are colour, odour, temperature, turbidity, density etc. Chemical aspects of pollution of water are dissolved solids, suspended solids, acidity, alkalinity, pH, dissolved oxygen, heavy metal ions, anions, pesticides and other organic pollutants. Biological water pollution may occur due to the presence of harmful disease causing bacteria, algal blooming and due to decomposition of animal and plant matter.

Water pollution mainly occurs due to industrial activities and agricultural activities. Water pollutants can be categorized as point sources and non-point sources. A point source is a single identifiable source of pollution which results when the contaminants come from a single location. Hazardous spills, underground storage tanks, storage piles of chemicals, mine-waste ponds, deep-well waste disposal, industrial or municipal waste outfalls, leachate from waste dumpsites and septic tanks are some examples for point source pollutants. Non-point source pollution results when contaminants are introduced into the environment over a large widespread area. In non-point source pollution, a single source which causes pollution is difficult to recognize. Storm drainage, urban and industrial runoff, farm runoff, waste water from construction sites and other land disturbances are considered as nonpoint sources. When storm drainage which is contaminated with harmful substances and chemicals, and farm runoff which is contaminated with pesticides, fertilizers and animal manure, passes through other surface areas it contaminates the land and water bodies and therefore causes diffuse pollution. So, as a result it is more difficult to monitor and control non-point source pollution due to the heterogeneity of soil and water systems at large scales and also it may result in long term, chronic (and endocrine) effects on human health and soil-aquatic degradation. On the other hand, point source pollutants are easier to control and are

more readily identifiable and measurable compared to nonpoint source pollutants, but point source pollutants are generally toxic [2].

There are many types of pollutants. Different types of pollutants such as inorganic compounds, synthetic organic compounds, pigments, dyes, metal ions, acids and bases, pathogens, fertilizer and pesticides are added to the natural water due to industrial and anthropogenic activities. These pollutants cause significant damage to the equilibrium of the ecosystem. Potential sources of ground water contaminants are shown in Table 1.1. However, the effect of pollutants depend on the type of pollutant, concentration of pollutants and the duration of exposure to the community.

Table 1.1: Potential sources of ground water contaminants

Source	Possible contaminants
Accidental spills	Various inorganic and organic contaminants
Acid rain	SO_2, NO_2
Agricultural activities	Fertilizers, pesticides, herbicides and fumigants
Animal feed	Organic matter, nitrogen and phosphorous containing compounds
Land fills	Heavy metals, gases, organic and inorganic compounds
Mining	Minerals and mining drainage
Leaching of septic tanks	Phosphorous containing compounds
Underground storage tanks	Organic cleaning, degreasing compounds, petroleum products and other hazardous waste

Considering many types of pollutants, heavy metals are known to be the most hazardous substances that aid water pollution. Electroplating, leather tanning, paint, textile, steel industries, mining, metal processing and battery manufacturing industries extensively release heavy metals to the natural water bodies [2]. Since heavy metals are considered as conservative pollutants, they are not subjected to decomposition or degradation processes which promote them to accumulate in water bodies. This leads to bioaccumulation of heavy metals in food chains [3].

When this occurs in higher organisms, various diseases and disorders would result in even at minute concentrations [4]. Therefore, to evaluate water pollution, standard water quality parameters have been introduced by authorized bodies such as World Health Organization (WHO), European Union and United States Environmental Protection Agency (EPA). There are different guidelines on water quality parameters depending on the intended use. Table 1.2 depict standard drinking water parameters.

Table 1.2: Drinking water quality parameters & their desirable and permissible levels [5]

Parameters	**Highest desirable Level**	**Maximum permissible level**
Electrical conductivity at 25 °C (µS/cm)	750	3500
Total solids (ppm)	500	1500
Colour (Hazen Unit)	5	30
Taste	Unobjectionable	-
Odour	Unobjectionable	-
Turbidity (NTU)	2	30
Chloride (Cl^-) (ppm)	200	1200
Fluoride (F^-) (ppm)	-	1.5
Iron (Fe) (ppm)	0.3	1
Manganese (Mn) (ppm)	0.05	0.5
Copper (Cu) (ppm)	0.05	1.5
Zinc (Zn) (ppm)	5	15
Calcium (Ca) (ppm)	100	240
Magnesium (Mg) (ppm)	30	150
Total phosphates (PO_4^{3-}) (ppm)	-	2.0
Sulphate (SO_4^{2-}) (ppm)	200	400
Total alkalinity ($CaCO_3$)(ppm)	200	400
Total hardness ($CaCO_3$) (ppm)	250	600
Free ammonia (NH_3) (ppm)	-	0.06
Nitrate (NO_3) (ppm)	-	45
Nitrite (NO_2) (ppm)	-	0.01
Cyanide (CN^-) (ppm)	-	0.05

pH	Min 7.0; Max 8.5	Min 6.5; Max 9.0
Arsenic (As) (ppm)	-	0.05
Cadmium (Cd) (ppm)	-	0.005
Chromium (Cr) (ppm)	-	0.05
Lead (Pb) (ppm)	-	0.05
Mercury (Hg) (ppm)	-	0.001
Selenium (Se) (ppm)	-	0.01
Free residual chlorine (ppm)	-	0.2
Polynuclear aromatic hydrocarbons (ppm)	-	0.0002
Phenolic compounds (Phenolic OH) (ppm)	0.001	0.002
Greases and oil (ppm)	-	1.0
COD (Chemical oxygen demand) (ppm)	-	10
Radioactive materials		
Gross alpha radioactivity (pC/L)	-	3
Gross beta radioactivity (pC/L)	-	30

1.2 Industrial Uses of Heavy Metals

1.2.1 General Properties of Heavy Metals

Heavy metals are generally referred to the group of metals and metalloids whose density is 5 g cm^{-3} or more. They mostly are natural components of the Earth's crust and are available in natural environment in small concentrations. They take part in bio-geochemical reactions and are transported between compartments by natural processes.

Majority of heavy metals are stable at high temperature and high pressure due to their high melting point and most are resistant for corrosion. Due to the

presence of unpaired ‘d’ electrons, many heavy metals have magnetic properties and some metals form paramagnetic compounds.

Considering the biochemical properties of heavy metals, some heavy metals are required by most living organisms in small concentrations for healthy growth. Micro nutrients such as Cu, Mn, Fe and Zn are essential for both animals and plants while Co, Cr, Se and I are beneficial for animals and B and Mo for plants [6]. Most of these micro nutrients are essential constituents of enzymes and other important proteins which are involved in key metabolic pathways. Therefore, a shortage in such micro nutrients may lead to metabolic dysfunction causing diseases. However, heavy metals such as Hg, Pb, Cd, As, Cr, Ni, Cu etc. cause toxicities at concentrations when exceeds the tolerance level. Toxic levels of some heavy metals are just above the concentrations that are normally found in nature. Heavy metals can cause malfunctioning of the cellular processes via displacement of essential metals from their respective sites. Oxidative deterioration of biological macromolecules has been found to be primarily due to binding of metals to DNA and nuclear proteins [7].

Unlike other metals, heavy metals can be accumulated in living tissues as they are not subjected to decomposition or degradation processes [8]. This leads to bioaccumulation of heavy metals in food chains. Bioaccumulation means an increase in the concentration of a chemical, in a biological organism over time, compared to the chemical's concentration in the environment. When reached to a certain concentration, it causes damage and become toxic to living organisms. In higher organisms, various diseases and disorders would result in even at minute concentrations. *Minamata bay* incident and *itai-itai* disease are a couple of well-known incidents that occured due to heavy metals.

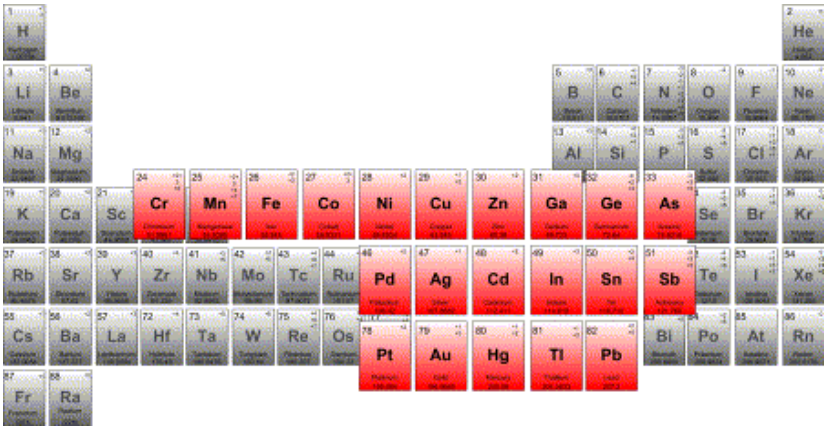

Figure 1.1: Periodic table showing major heavy metal elements

1.2.2 Heavy Metals in Industries

Heavy metals are widely used in structural applications. Iron is a prime example which forms steel, an alloy used in the structure of many modern machines and industrial products. Some of the heavy metals such as Nickel is often used as catalysts which are important in chemical industries. Conducting wires and tungsten filaments of bulbs are mainly made of Copper. Cadmium is used in industries, including pigment, ceramic, electroplating, fertilizers, mining and metallurgy. Zinc is widely used in alloys, galvanized steel and paint pigments. Iron, Cobolt and Nickel are used to create magnetic fields and magnets. Lead is used as a welding component of electric circuits and storage batteries and also used for the production of ink for printing industry. Mercury is used in electronic apparatus. Other than the above mentioned metals, almost all heavy metals are used in many industries.

1.2.2.1 Applications of Chromium

Chromium metal has a wide range of applications, mainly due to its hardness and resistance to corrosion. Chromium is used as a component for prevention of corrosion; for instance, in the manufacture of steel, stainless steel and alloys, and in metal plating. In the manufacture of stainless steel, chromium is used along with nickel, as it prevents corrosion and discoloration of steel. It is also used in improving other properties of metals. It also serves as a stable electrode material in batteries [9].

Acidic chromate or dichromate solutions are also used for surface coating. This is usually achieved with the help of electroplating, in which a thin layer of chromium is usually deposited on the surface of metals. However, for imparting wear resistance quality, a thick layer is required to be deposited, which is obtained by the chromate conversion coating process, through which chromates are used to deposit a protective layer on certain metals such as Al, Cd, Zn, Ag and Mg [10]. Chromium compounds are used to anodize aluminium, a process which coats aluminium with a thick, protective layer of oxide. Chromite, chromium's primary ore, is used to make moulds for firing of bricks because of its high melting point, moderate thermal expansion and stable crystal structure [11].

Salts of chromium are used in preserving wood from decaying, and damage caused by fungi, insects, termites, etc. owing to their toxic properties [12]. Cr(III) salts are also used in leather tanning. The high melting point and resistance to heat make chromite and chromium oxide ideal refractory materials. They have found applications in blast furnaces, cement kilns and metal casting [13]. Besides, many compounds of chromium are also used as catalysts. Chromium (VI) oxide is used to produce the magnetic component in audio tapes and cassettes [14]. In the field of pigments, Chrome yellow, made of lead chromate, was widely used as a pigment in the past. Other pigments of chromium include Chrome red, Chrome oxide green and Chrome green, which are mixtures of Chrome yellow and Prussian blue [15, 16]. Chromium oxide is used for imparting greenish colour to glass. Besides, emeralds also owe their green tint to the effect of chromium. Chromium oxide is also used in manufacturing synthetic rubies [17].

Chromium is a trace mineral, essential as a nutrient to man and animals [18 – 21]. Cr(III) is required in human body in very small amounts. It is mainly required for carrying out lipid and sugar metabolism. Nowadays, chromium is used in many dietary supplements claiming to have several health benefits [22]. But, some compounds of chromium can be harmful to health, and thus they should be avoided. For example, chromium metal and any other chromium compounds are toxic. They have been exhibiting carcinogenic properties. Chromate salts (CrO_4^{2-}) have also been found to induce allergic reactions in some individuals [23, 24]. Due to these health and environmental issues, restrictions have been imposed on the use of certain chromium compounds in many countries.

1.2.2.2 Applications of Copper

Copper is one of the metals that had been used since early stages of human evolution. Nowadays, copper is widely used in industries even though it belongs to the group of seriously hazardous heavy metals [25]. At the same time, copper ion is an essential nutrient to higher plants and animal life, where it acts as a cofactor of enzymes and as an antimicrobial agent [26]. Few copper containing compounds, such as copper metal, copper sulphate, copper oxides and copper chloride, are used in commercial industries.

As a pure metal, copper is mainly used in power generation, transmission and telecommunication industry, building industry, machinery, and vehicle industry. In power transmission and telecommunication industry, it is used to print circuit boards, production of electric transmission wires and to build the inner parts of dynamos and motors. In electroplating industry, copper is used due to its anti-corrosion property. Copper pipes are used to conduct heat in refrigerators and air conditioners. Copper and its alloys are used to build connectors, brakes, radiators and bearings in vehicle industry.

Copper alloys with different types of properties are useful in many industries. For example, brass, made out of copper and zinc, has antimicrobial, electrical and thermal conductivity and corrosion resistant properties. Brass is used in instruments, coins, door locks, bolt, to decorate house hold items, etc. Bronze, gunmetal, nickel-silver, beryllium-copper are some other alloys that are made out of copper. Among these beryllium-copper is the hardest and strongest.

Copper sulphate-penta hydrate is commonly used in agricultural purposes as fungicides, algaecides and plant nutrients. It is also used as a blue and green pigment in dyes, as a print toner in photography and in leather tannin. Copper oxide is used in wood preservation. Copper carbonate which was earlier used as a precursor in the production of high surface area catalyst in feed industry is replaced by zinc carbonate [26].

1.2.2.3 Applications of Zinc

Zinc is the fourth most widely used metal in the world [27]. It is naturally present in rock, soil and water, and always occurs with the minor metal cadmium. It is an essential element and a nutrient for biological systems. In human body, it is important for several enzymatic reactions as a co-factor and an activator [28]. Zinc widely occurs by combining with silicon, sulphur and oxygen. More than 50 countries, including Canada, USA, China and Australia, mine zinc ores [29].

The major use of zinc in the world is galvanizing**.** As zinc is less susceptible to corrosion, a thin coat of zinc is electroplated on steel in order to prevent corrosion in galvanizing. Zn is also used to make brass combining with copper. Another significant use of zinc is the production of zinc oxide which is used as a protective

skin ointment in rubber manufacturing. Zinc oxides are used in paint pigments, lotion and creams to prevent sunburn [27].

1.2.2.4 Applications of Lead

Lead is the fifth most widely used metal in worldwide industries and the common mineral source of lead is galena or lead sulphide. Since the melting point of lead is relatively low (327 °C), it is allowed to be readily worked. Lead is a major component in storage batteries which is the greatest use of lead in worldwide, for example elemental lead and lead oxide is employed as the two electrodes in storage batteries in almost all vehicles.

Lead salts are greatly used as glazes and pigments. Lead oxide which is yellow solid is used to glaze pottery. Currently lead silicates rather than oxides or sulphates are used in glazing since it is almost insoluble and much safer. Lead chromate is another yellow pigment used to paint strips on roads, buses, etc. Pb_3O_4 (red lead) is used as a corrosion resistant paint and has a bright red colour, which used in great quantities in past to produce rust-resistant surface coating for iron and steel. Lead acetate is often used for the preparation of dye which is used to colour gray hair. $Pb_3(CO_3)_2(OH)_2$ (White lead) was used widely as a major component of white indoor paint. It was used to paint kitchen cabinet, windows and other indoor surfaces because of the durability than other paints. However, now it has been replaced by pigment TiO_2, but continues to be used for exterior paints [30].

For radiological protective clothing lead powder itself or lead oxide is used. And also it is used to produce cathode ray tubes and anti-friction products. Lead is also used as stabilizers in variety of PVC products. Lead incorporated plastics can undergo partial decomposition from exposure to UV in sunlight. Due to the high density of lead, it is used as a very effective structural material for roofing, for sound proofing and weatherproofing. Hunters use lead incorporated bullets (lead shots) in hunting. Furthermore, lead arsenate is used as a pesticide [30].

1.2.2.5 Applications of Nickel

Compared with other materials, nickel-containing products possess better corrosion resistance, greater toughness, more strength at high and low temperatures,

and a range of special magnetic and electronic properties. Therefore, most nickel production is used for alloying elements, coatings, batteries, and some other uses, such as kitchen wares, mobile phones, medical equipment, transport, buildings, power generation and jewellery [31].

Nickel can alloy with steel, iron, copper, chromium, aluminum, lead, cobalt, silver, gold and other elements to make stainless steel, cast iron, inconel, incoloy, monel, nimonic and other alloys. Nickel-base alloys include Ni-base superalloy, Ni-base corrosion resistant alloy, Ni-base wear-resistant alloy, Ni-based precision alloy, Ni-base shape memory alloy and Hydrogen storing alloy. The above alloys are widely used in aviation, shipbuilding, the chemical industry, electronics, medicine and the energy industry. Nickel powder is used for powder metallurgy (P/M) alloys [32].

Nickel coatings primarily refer to electroplated nickel, which is used to provide hard-wearing decorative and engineering coatings as 'nickel-plating' or 'electroforming'. When used with a top layer of chromium, it is popularly known as 'chrome-plating'. When done in combination with silicon carbide it is known as composite plating, such as in the coating of coins. Nickel is a key part of several rechargeable battery systems used in electronics, power tools, transport and emergency power supply. The most important application is nickel-metal hydride (NiMH) [31, 32].

1.2.2.6 Applications of Cadmium

Cadmium is a poisonous metal and its use is somewhat limited for this reason. Like Zinc, Cadmium can be electroplated to other materials to protect them from corrosion. Cadmium easily absorbs neutrons and is used to make control rods for nuclear reactors. Cadmium is also used in rechargeable nickel-cadmium batteries [33].

Cadmium is alloyed with silver to form solder, a metal with a relatively low melting point used to join electrical components, pipes and other metallic items. Cadmium based solders must be handled with care to prevent cadmium poisoning. Cadmium alloys are also used to make low friction bearings that are highly resistant to fatigue. Hydrated cadmium sulfate ($3CdSO_4 \cdot 5H_2O$), one of cadmium's compounds, is used in a device called a Weston cell, a type of battery that produces

a precise voltage used to calibrate medical and laboratory equipment. Cadmium sulfide (CdS), another cadmium compound, is a yellow powder that is used as a pigment. Other cadmium compounds are used in the phosphors of black and white television sets and in the blue and green phosphors in color television sets [34].

1.3 Heavy Metals and Environment

Heavy metals and their ions in the environment have different sources of origin. After releasing to the environment, they find many path ways depending on their affinity towards different components of the surrounding [35]. Most of the heavy metals show adverse effects on many components of the ecosystem, due to their ability of travelling long distances in the atmosphere before they are deposited. Heavy metals are added to the environment not only due to anthropogenic activities, such as industries, pesticides and fertilizers, but also due to geological origins. As heavy metals are non-degradable, they can be found in air, soil and water. Since plants absorb nutrients and water from the soil, heavy metals in the environment can easily enter plant bodies. Heavy metals present in water bodies also enter living organisms. Consumption of such organisms leads to bioaccumulation and biomagnification of the heavy metals in higher members of the food chain [36]. Thus, the fate of heavy metals can be ended up in any component of the ecosystem.

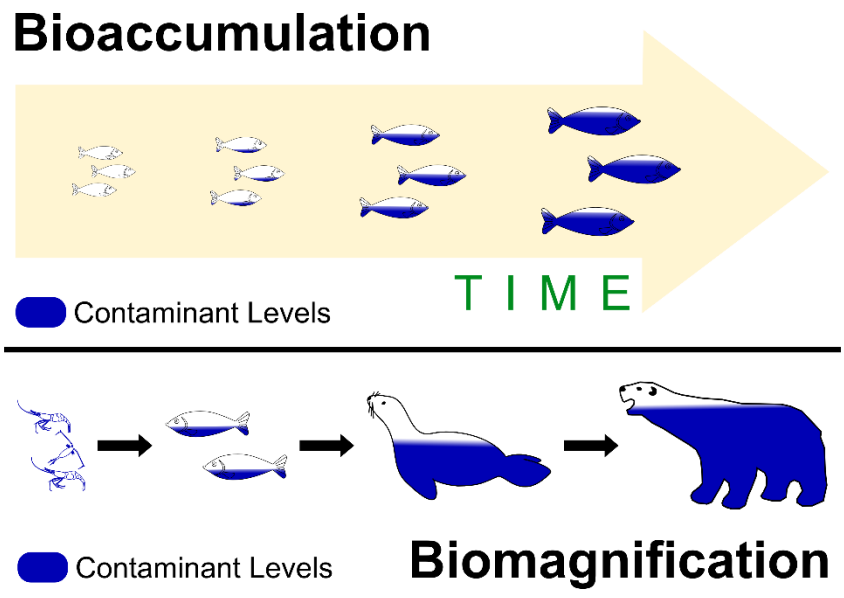

Figure 1.2: Bioaccumulation and biomagnification [37]

1.3.1 Heavy Metals in Water and Soil

Heavy metals are released into water bodies through industrial effluents. Further, metal ions that are suspended in the atmosphere tend to move into water bodies. Consequently, heavy metals react with other constituents in water, bind to soil sediments or get deposited on the bottom of water bodies. The solubility of heavy metal ions depends upon several factors, such as, anions present in the environment, chelating agents, pH of water and the presence of adsorbents.

In alkaline environments, heavy metals are co-precipitated by several metal hydroxides, such as Fe, Mn and Al [38]. Iron hydroxides co-precipitate with Cd, Cu, Pb and Zn in alkaline media leading to the accumulation of metals in the sediments [39]. Aluminium hydroxide co-precipitates arsenate, a highly toxic metalloid, in the environment [40]. Calcium carbonate, an abundant mineral in limestone rocks, adsorbs heavy metals such as Ni, Zn, As and Cd in natural water bodies [41]. Different clay minerals present in soil sediments also adsorb heavy metals, such as V, Ni, Co, Zn, Cu and Cr, present in the natural water flows [38, 42]. When these factors are considered, it is clear that some amounts of the heavy metals contained in natural water bodies are settled with soil sediments while the rest remains in the water phase.

Soil is composed of different amounts of clay and organic compounds having ability to immobilize from sorption processes. Main factors that affect sorption mechanisms are pH, moisture content, temperature, soil organic matter content, clay fraction, and the nature of metal ions [43]. As a result, heavy metals, such as Fe, Cr, Mn, Ni, Zn, Cu, Pb, Cd and Hg, are immobilized in soil.

Acidity of the soil is one of the major factors that affects heavy metal sorption by the soil which is highly influenced by anthropogenic activities, such as acid rains and agrochemical usage [44]. When the acidity of soil increases, the mobility of heavy metal ions is increased as compared to alkaline and neutral pH [45]. The mobility of heavy metal ions is also highly affected by the type of organic matter present in the soil. This can be explained by considering the negatively charged clay materials which are formed due to the hydroxyl ions present on the outer layers. The hydrogen bound to oxygen is not very tight; thus, when pH of the soil increases they can easily be replaced by other cations, such as Cs^{2+}, Pb^{2+}, Cd^{2+} and Al^{3+}.

The second major factor that affects heavy metal sorption in soil is the organic matter content. Soil organic matter contains decayed plant and animal tissues, their partial decomposition products and soil bio mass. High organic matter content in soil results, high cation exchange capacity, high moisture content and high buffering properties of soil which leads to immobilization of heavy metals. During temperate climates, where soil reflects high organic matter decomposition, soils contain small organic molecules and stable insoluble humic substances which act as ligands for many metal ions [44, 45].

1.3.1.1 Chromium in Water and Soil

Chromium is present in water mainly in two oxidation states, Cr(III) and Cr(VI). However, chromium is naturally available as Cr(III), and mined as chromite ($FeCr_2O_4$) [46].Cr(VI) is readily soluble in water than Cr(III). Therefore, Cr(VI) is present in industrial waste waters in larger amounts as compared to Cr(III). The relative concentrations of Cr (VI) species, $Cr_2O_7^{2-}$ or CrO_4^{2-}, depend on the pH of the medium. Therefore, to study the interaction of Cr(VI) with natural systems, is very important when designing treatment procedures of industrial effluents.

Cr(VI) is reduced to Cr(III) chemically in the presence of reducing agents, such as Fe^{2+}, sulphide or by microorganisms *Saccharomyces* species (yeast) [47]. In biological systems, Cr(VI) is reduced by many ways [48]. In addition to reduction, Cr(VI) forms complexes with natural substances, such as silica and other soil components, and further, it is adsorbed on many natural substances [49].

Rates of chromium uptake from the gastrointestinal tract are relatively low. These rates depend on a number of factors, including the oxidation state [with Cr(VI) more readily absorbed than Cr(III)], the chemical form (with organic chromium more readily absorbed than inorganic chromium), the water solubility of the compound and time of exposure. Once absorbed into the bloodstream, Cr(VI) is rapidly taken up by erythrocytes and reduced to Cr(III) inside the red blood cells. In contrast, Cr(III) does not readily cross red blood cell membranes, but binds directly to transferrin, an iron-transporting protein in the plasma [50, 51].

Reduction of Cr(VI) in red blood cells occurs by the action of glutathione. Since the red blood cell membrane is permeable to Cr(VI) but not to Cr(III), the Cr(III) formed by reduction of Cr(VI) is essentially trapped within the red blood

cell. Eventually the diffusion of Cr(VI), its reduction to Cr(III), and complexing to nucleic acids and proteins within the cell cause the equilibrium concentration to change. Regardless of the source, Cr(III) is widely distributed in the body and accounts for most of the chromium in plasma or tissues. The greatest uptake of Cr(III) as a protein complex is via bone marrow, lungs, lymph nodes, spleen, kidney and liver. Autopsies reveal that chromium levels in the lungs are consistently higher than those in other organs [52].

The first defense against Cr(VI) after oral exposure is the reduction of Cr(VI) to Cr(III) in the gastric environment, where gastric fluid and ascorbate play important roles [52-54]. Excretion of absorbed chromium occurs primarily via urine. In humans, the kidney excretes about 60% of absorbed chromium dose in the form of Cr(III) within 8 hours of ingestion. Approximately 10% of an absorbed dose is eliminated by excretion, with smaller amounts excreted in hair, nails, milk and sweat [52, 55]. Clearance of Cr(III) from plasma is generally rapid (within hours), whereas elimination from tissues is slower (with a half-life of several days). Cr(VI) is better absorbed from the lungs, gut and skin than Cr(III). The difference in bioavailability and bioactivity between Cr(III) and Cr(VI) might account for the differences in toxicity [56].

High concentrations of Cr(VI) in soil are found in bottom sediments of water reservoirs contaminated with tannery waste, dust from a sanitary landfill of chromate compounds and transported chromium products, while Cr(III) is retained preferentially in the superficial soil layer [57]. It has also been found that chromium is attracted preferentially to hydrous Fe and Mn oxides in more polluted soils, and less polluted soils have a high proportion of chromium associated with the sulfide and organic fraction. Further, factors such as variations in the physical characteristics of the soil, relative abundance of the various soil components and characteristics of the contaminant source, give rise to differences in chromium concentrations in soil with depth [58].

If Cr(VI) is reduced to Cr(III) extracellularly, this form of ion is not readily transported into cells so toxicity is not observed. The balance that exists between extracellular Cr(VI) and intracellular Cr(III) is what ultimately dictates the amounts and rates at which Cr(VI) can enter cells and impart its toxic effects.

Harmful effects arise due to Cr(VI) exposure can be summarized as follows [59],

• When inhaled, chromium compounds are respiratory tract irritants and can cause pulmonary sensitization.
• Chronic inhalation of Cr(VI) compounds increases the risk of lung, nasal, and sinus cancer.
• Severe dermatitis and usually painless skin ulcers can result from contact with Cr(VI) compounds.
• DHHS, EPA, WHO, and IARC have all recognized Cr(VI) as a human carcinogen.
• Occupational exposure to Cr(VI) compounds in a number of industries has been associated with increased risk of respiratory system cancers.
• Some studies indicated that reversible renal tubular damage can occur after low-dose, chronic Cr(VI) exposure. (Occupational exposure to Cr(III) does not appear to be associated with renal effects)
• Cr(VI) compounds can cause mild to severe liver abnormalities.
• Some Cr(VI) compounds, such as potassium dichromate and chromium trioxide, are caustic and irritating to gastrointestinal mucosal tissue
• Ingestion of a lethal dose of chromate can result in cardiovascular collapse.
• Oral exposure to Cr(VI) compounds may result in haematological toxicity.
• Data indicate that Cr(VI) compounds are teratogenic in animals.
• Cr(VI) compounds induced DNA damage, gene mutation, sister chromatid exchange, chromosomal aberrations in a number of targets, including animal cells in vivo and animal and human cells in vitro.

1.4 Polyaniline / Coconut Coir (PANI/CC) Composite

1.4.1 Polyaniline

Polymers containing hetero atoms such as oxygen and nitrogen have been used as adsorbents to purify water (Ex: Chitosan and pure coconut coir) [60]. Due to the presence of nitrogen atoms along the polymer backbone, polyaniline can be used as an adsorbent to adsorb heavy metal ions from wastewater.

PANI can be easily synthesized due to wide availability of chemicals/reagents needed and the employability of easy methods for the synthesis [61, 62]. There are two main methods for the polymerization process of aniline to form PANI. First method is *electrochemical polymerization process* which is commonly carried out by employing one of following three techniques. Three techniques could be employed to do the electrochemical polymerization; (i) a constant voltage (potentiostatic), (ii) a variable current and voltage (potentiodynamic) and (iii) a constant current (galvanostatic) to an aqueous solution of aniline [63]. Upon carrying out electrochemical polymerization using any of the above techniques, a three electrode system should be employed. The three electrode system is composed of counter electrode, reference electrode (e.g. Ag/AgCl) and working electrode. Here the electro-synthesized polymer is deposited on the working electrode, which is commonly FTO or ITO glass substrate. The electrolyte medium used for the electrochemical polymerization is an acidic (HA) medium in order to provide sufficient low pH to solubilize aniline monomer in water and to avoid excessive branching of undesired products. In addition, low pH of the system helps to generate the doped emeraldine salt (ES) form, which is the conductive form of the emeraldine base (EB) [64].

Second method is *chemical polymerization process*. In chemical polymerization, monomers have to be oxidized to initiate the reaction. $(NH_4)_2S_2O_8$ which has oxidation potential E_0 = 1.94 V and $FeCl_3$ with E_0 = 0.77 V are the most commonly used oxidizing agents [65]. Similar to electrochemical polymerization, acidic pH conditions (pH < 3) are required for chemical polymerization as well. The low acidic pH leads to lesser formation of undesired branched product [66]. Since chemical polymerization is employed in this study, more focus is given about

the chemical polymerization of the aniline. The mechanism of the chemical polymerization process is shown in Figures 1.4 – 1.7.

Step 1: Oxidation of Monomer

In the initial step, as shown in Figure 1.4, the oxidation of aniline to a radical cation is occurred. This formed radical could be existed in three resonance forms. This step is the slowest step in the reaction, hence it is the rate determining step in aniline polymerization [67].

$$2e^- + S_2O_8^{2-}{}_{(aq)} \longrightarrow 2\ SO_4^{2-}{}_{(aq)} \qquad \text{(Reduction half reaction)}$$

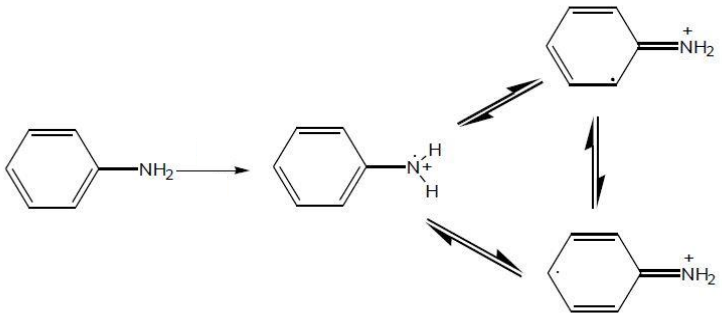

Figure 1.3: Oxidation of monomer during polymerization of aniline

Step 2: Radical coupling and re-aromatization

Head to tail coupling of the *N*- and *para*- radical cations (Figure 1.5) takes place, resulting a dicationic dimer species. Then this dimer further undergoes the process of re-aromatization, yielding an intermediate referred to as *p*-aminodiphenylamine (PADPA). This process is accompanied by the elimination of two protons.

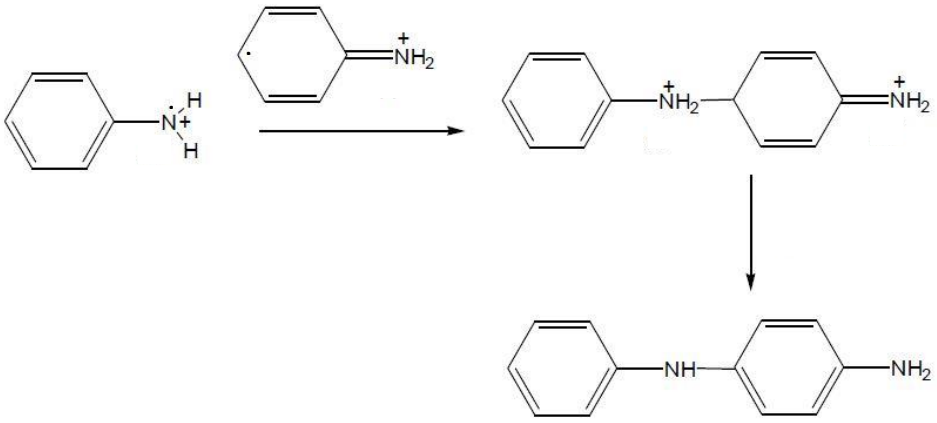

Figure 1.4: Radical coupling and re-aromatization during polymerization of aniline

Step 3: Chain propagation

In the chain propagation during the chemical synthesis of polyaniline, the initial product is the fully oxidized to pernigraniline salt as shown in Figure 1.6 below.

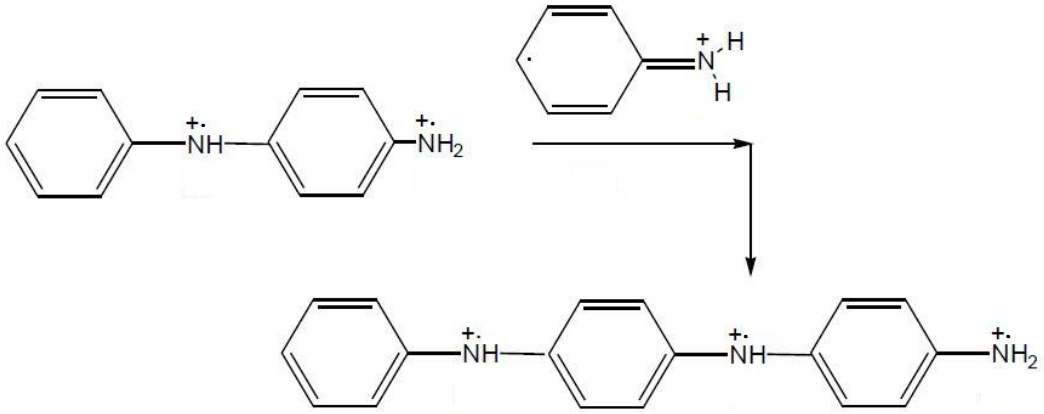

Figure 1.5: Chain propagation of the polymer during polymerization of aniline

Step 4: Reduction of the pernigraniline salt to emeraldine salt

When all the oxidizing agents in the reaction mixture is completely used up, the pernigraniline salt formed in step 3 of the chemical synthesis mechanism is reduced by unreacted aniline monomer to the green emeraldine salt (Figure 1.7).

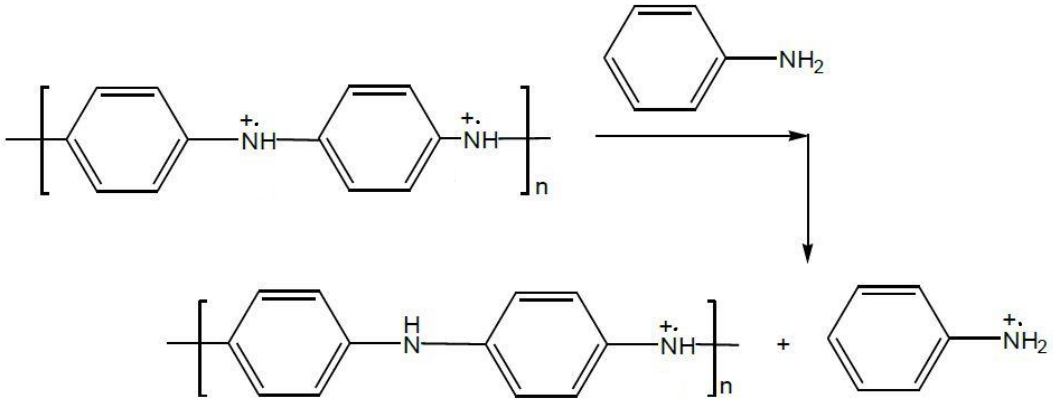

Figure 1.6: Reduction of the pernigraniline salt to emeraldine salt during polymerization of aniline

Depending on the level of oxidation the polymer it can be synthesized a mixed oxidation state polymer consisting of benzoid and oxidized quinoid units, average oxidation state of PANI is denoted by 1-y where the value of y changes the structure of the polymer formed. There are three distinct PANI oxidation states as shown in Figure 1.8. Thus PANI exists as fully reduced leucoemeraldine (LE) where 1-y = 0, half oxidized emeraldine base (EB) where 1-y = 0.5 and fully oxidized pernigraniline (PE) where 1-y = 1. Since EB is showing the highest stability at room temperature, it is regarded as the most useful polymeric form of PANI. EB is composed of two benzoid units and one quinoid unit that alternatively positioned in the polymer chain, and this EB form shows characteristics of semiconductor.

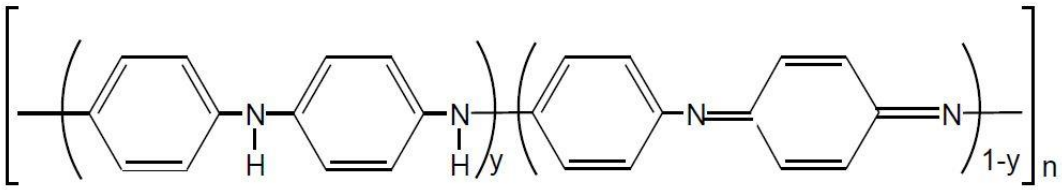

Figure 1.7: Different oxidation states of polyaniline (y = 1: leucoemeraldine, y = 0.5: emeraldine and y = 0: pernigraniline

PANI chain can be formed by various combinations of the two repeating units with the change in the value of y. Due to this, PANI has many unique properties and electronic conduction mechanisms that highlights it from the rest of the conducting polymers. For an example with the extent of oxidation (variation in the number of electrons) and the degree of protonation (variation in the number of protons) the conductivity of PANI varies.

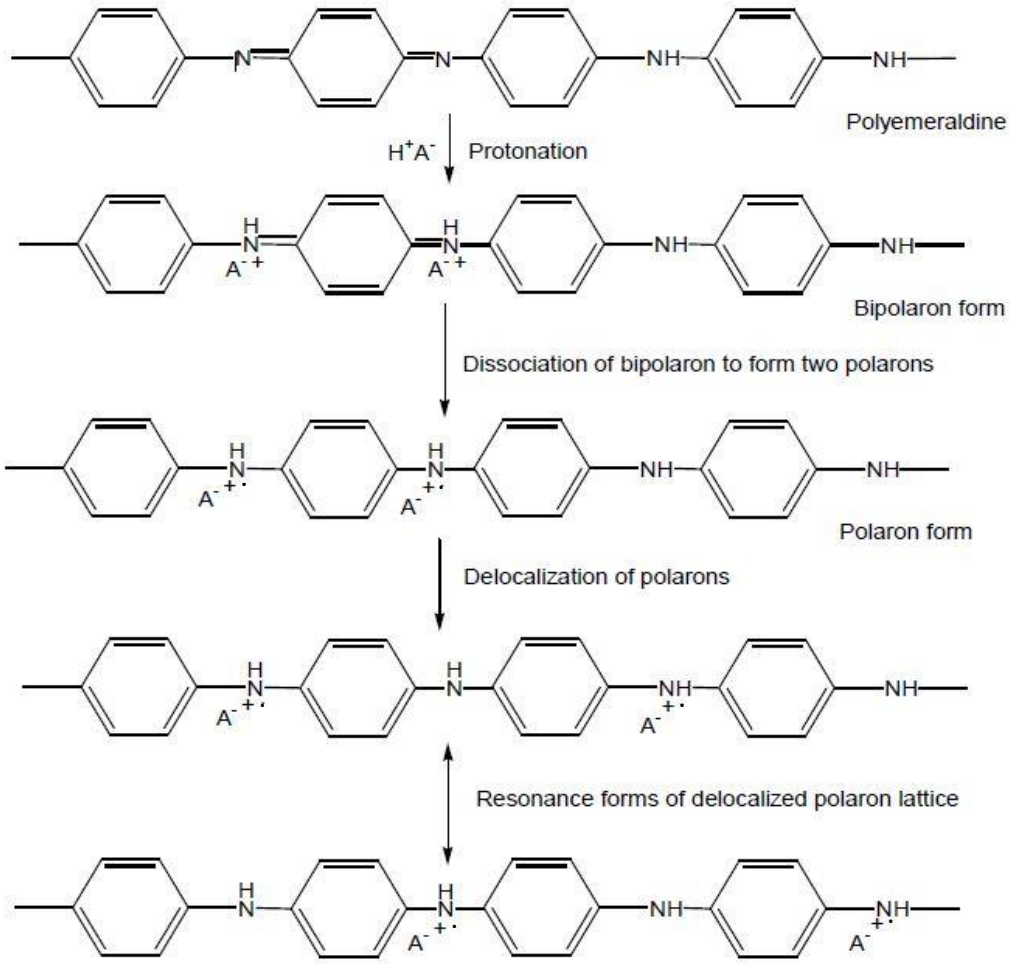

Figure 1.8: The doping of EB with protons to form the conducting emeraldine salt (PANI/HA) form of polyaniline

Among the various oxidation states of PANI, EB is the one that can be doped to higher level of conductive state. In EB form of PANI, the structure is consisted of equal proportions of amines (–NH–) and imine (=N–) sites. Through protonic acid doping, imine sites are protonated by acids HA to the bipolaron (dication salt) form. The bipolaron formed then undergoes a further rearrangement

to form the delocalized polaron lattice which is a polysemiquinone radical-cation salt as shown in Figure 1.9 [67].

1.4.2 Coconut coir

Coconut coir is a light brown to dark brown colour fluffy material which falls off from coconut husk when it is shredded during coir processing [68, 69]. It is primarily produced in Sri Lanka, India, Philippines, Indonesia, Mexico, Costa Rica, and Guyana [70]. Coconut coir is about 70% of the weight of the coconut husk. This fall off material is available as a waste product since it has no industrial value [71]. During recent years, coconut coir is used as a soilless growing media for ornamental plants [72]. Coconut coir has also been used as a sorbent to remove heavy metals ions [73].

Coconut coir contains approximately 36% (w/w) cellulose and 54% (w/w) lignin [69]. Since it consists of high amount of cellulose and lignin with low ash content, coconut coir is characterized as lignocellulosic material which is hygroscopic having the affinity for water. Further, coconut coir is rich in tannins, hemicellulose and pectin [74]. Physical properties of coconut coir such as water supply and availability, areation and relative hydraulic conductivity strongly depend on the particle size [75].

Cellulose and hemi cellulose have a large fraction of carbohydrates. Cellulose is the most abundant and a renewable polymer resource. Cellulose and hemicellulose are biopolymers which consist of numerous (-OH) groups, which are useful in enhancing chemical reactivity. Lignins are aromatic polymeric compounds which consist of various functional groups, such as hydroxyl, methoxyl and carbonyl, which give high polarity [74].

The carboxylate and phenolic groups of lignin, pectin and hemicellulose are known as the main sites for metal binding where the bonds are predominantly of covalent character. According to the structure and composition of coconut coir, it can be stated that more than one component of lignin, cellulose and hemicellulose are responsible for bonding. Since the exchange sorption properties of coconut coconut coir is due to the presence of some functional groups, such as carboxylic, hydroxyl, phenolic and lactone groups, which have a high affinity for metal ions.

1.5 Methods of Removal of Chromium

1.5.1 General Aspects on Heavy Metal Removal

Water treatment technologies, which are currently used, involve chemical precipitation, evaporation, electrochemical treatment and use of ion exchange resins etc. These methods are expensive and sometimes ineffective, especially when metals are present in solution at very low concentrations [76-78]. Several conventional techniques, including adsorption, electrochemical precipitation and reverse osmosis are still used for treatment of effluents containing metal ions [79-81]. However, effective methods, based on the introduction of synthetic chemicals, have become attractive as reliable means of removing toxic heavy metals from the environment despite their drawbacks, such as high cost and not being environmentally friendly [82-84].

Table 1.3: Advantages and disadvantages of some heavy metal removal methods

Technology	Advantages	Disadvantages
Chemical precipitation	Process simplicity Not metal selective Inexpensive capital Inexpensive equipment requirement Convenient and safe operations	High sludge production High cost for sludge disposal, chemical reagents and for maintenance
Ion exchange	High metal selectivity High removal efficiency Produced sludge volume is less Limited pH tolerance	High initial capital cost and operational cost
Membrane filtration	Low solid waste generation and low chemical consumption Small space requirement Increase heavy metal removal efficiency Can be used for large scale applications	High initial capital cost and high maintenance cost Membranes cannot be used at high temperatures

Adsorption	Low cost High efficiency Minimization of chemical or biological sludge Wide variety of target pollutants Environmental friendly Possibility of metal recovery	Relatively high capital cost Difficulty in separation of biosorbents after adsorption Performance depends on type of adsorbent

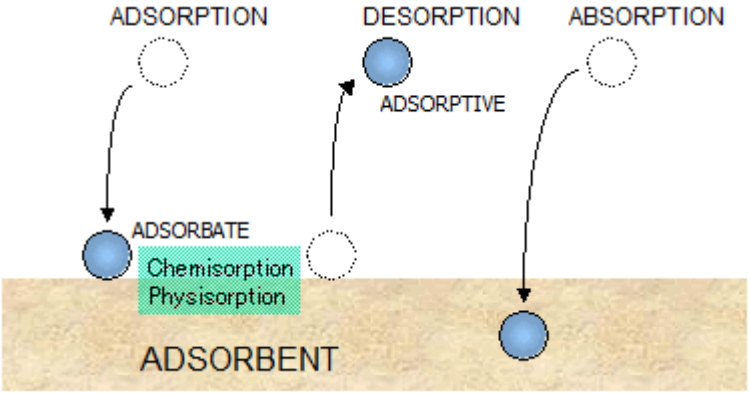

Figure 1.9: Adsorption, desorption and absorption procesess

Due to introduction of rigorous environmental regulations, tolerance limits for heavy metals in drinking water and wastewater has become more and more strict. Economical and green approaches have become a must in developing alternative pollutant removal methodologies. Consequently, removal of toxic substances by the use of chemicals has become a great concern now. This could be made limited if natural, environmentally friendly and low-cost substances are introduced. Among them, naturally occurring clay minerals and saw-dust having strong ion exchange properties have been attempted by many researchers as viable alternatives to chemical adsorbents for effective removal of inorganic pollutants [85, 86]. Excellent capacity of adsorption, surface specificity and porosity are among many desirable properties of clay minerals toward the removal of chemical pollutants from the environment [87].

Another approach that is becoming widespread in the area of heavy meal removal is the use of biologically active materials (biosorbents). Searching for plants which possess the natural ability to uptake heavy metals for the remediation of the environment has already become an emerging field of interest. Besides live plants, studies have demonstrated that dead plant biomass can effectively bind toxic metals, and therefore, such substances can also be used to remove metals from

solution [88]. The unique ability of some plants to bind metals has been attributed to the presence of various functional groups, such as –OH group, which can from complexes with metal ions. This technology is attractive mainly because it is effective, environmentally friendly and inexpensive.

Screening experiments performed for the removal of metal ions by desert plants indicated that *Solanum elaeagnifolium* (silver leaf nightshade) had the potential to be used as a biomaterial for heavy metal removal from contaminated soils and waters [89]. The inactivated biomass of *Solanum elaeagnifolium* is shown to be capable of binding several metals, such as, Pb (II), Cu (II), Ni (II), Cd (II), Zn (II), Cr (III) and Cr (VI). Metal ion binding is found to be rapid, indicating that the metals are probably adsorbed to the cell walls of plant tissues. Also, metal ion binding is found to be pH-dependent, suggesting the involvement of carboxyl groups present on the cell walls. Chemical modification of the biomass with NaOH enhanced metal binding, further supporting this hypothesis [90].

The methods for removal of heavy metals by soil particles have also become an area of current research, because these methods are economical and effective. Among many components in soil, minerals are more responsible for metal ion removal. The extent of interaction of a metal ion with a mineral surface depends on many factors, such as solution pH, surface acidity, type of pre-treatment, exposure time and temperature of interaction. These interactions are also controlled by the presence of other ions, organic matter and microbes, which would form thin films on mineral surfaces [91]. In a recent study, heavy metal removal has been investigated using a silicate colloid, prepared by the hydrolysis of tetraethoxysilane and NH_4OH (30%), followed by modification with (3-mercaptopropyl) trimethoxysilane [92]. The modified colloid has been able to adsorb heavy metals, such as Pb and Cr, from effluents. After adsorption, the colloids can be separated by coagulation of aluminum sulfate.

1.5.2 Chromium Removal

As the surface of many soil types is negatively charged, attraction between Cr (VI), present in the anionic form ($Cr_2O_7^{2-}$ or CrO_4^{2-}), and soil particles is very low due to electrostatic repulsion between two negatively charged species. However, the removal of Cr (III), present as cations, by negatively charged

substances is strong [93]. In addition to direct adsorption, another approach to detoxify Cr (VI) from waste water is its reduction by bacteria-generated reducible species, such as sulfide or ferrous irons [94]. Surface catalyzed chemical reduction of Cr (VI) by metal oxides and low molecular weight organic substances have also been reported [95]. Further, many clay minerals, including kaolinite, montmorillonite and SiO_2, are found to inhibit the sulfide reduction of Cr (VI) to various degrees [96]. This reaction is, however, activated by elemental sulfur that is formed during the oxidation of sulfide. In these attempts, susceptibility of Cr(III) to oxidation is a concern if all chromium species are not completely and irreversibly removed by the system employed. Additionally, pre-treatment methods of adsorbents to increase the Cr(VI) removal ability have also been recently reported [97].

The equilibrium concentration of Cr(VI) in soil systems containing low molecular weight organic acids, such as oxalic and tartaric, is significantly affected by pH, suggesting that the toxicity of Cr (VI) in soil environments is a complex issue [98]. The chemical reduction of Cr(VI) by sulfides in aqueous kaolinite suspensions was found to be of second order with respect to H^+, while it is of first order with respect to Cr (VI), the major reactant, demonstrating the active involvement of H^+ for Cr (VI)-kaolinite interactions [99]. The above observations and other reports on interactions of Cr(VI) with different substrates demonstrate the complexity of heterogeneous systems [100].

1.6 Sorption and Kinetics Studies of Heavy Metal Adsorption

1.6.1 Equilibrium Studies

The removal of heavy metals using adsorption is an adsorbent - adsorbate interaction process. When a mass of adsorbent and a metal solution are in contact for a sufficient time period, equilibrium occurs between the adsorbate in the aqueous phase and the adsorbent. In order to investigate the amount of metal ions adsorbed by a certain adsorbent, equilibrium models are used. This distribution of metal ions between the solution and the sorbent can be expressed by one or more isotherms [101]. Equilibrium isotherm data obtained from different models provide information about adsorption mechanisms, surface properties of the adsorbent and

affinities of the adsorbent [102]. Further, when evaluating these adsorption processes as unit operations, the physicochemical data obtained from sorption equilibria are involved.

Number of isotherm models are used to characterize adsorbate-adsorbent systems, such as Langmuir, Freundlich, Tempkin, Dubinin–Radushkevich and Redlich-Peterson. Among these, Langmuir and Freundlich models are the mostly fitted models for biosorbents [103]. Langmuir adsorption isotherm is based on four major assumptions; molecules are adsorbed to a finite number of identical sites; each site can allocate one adsorbate molecule; all sites are energetically equivalent; there are no interactions between molecules adsorbed on adjacent sites [104]. According to the Langmuir adsorption isotherm, the sorption occurs on a homogeneous surface resulting in the formation of a monolayer of the adsorbate [101, 104]. The mathematical equation of Langmuir model can be written as,

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \tag{1.1}$$

where q_e is the amount of metal adsorbed at equilibrium (mg/g), q_{max} is the monolayer sorption capacity (mg/g), K_L is Langmuir constant (dm^3/mg), C_e is concentration of metal ion in solution at equilibrium (ppm). The linear form of this can be given as,

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{K_L q_{max}} \tag{1.2}$$

Further, Langmuir model can be used to calculate the specific surface area of monolayer coverage of a certain metal ion on a specific adsorbent [105]. By plotting a graph of log K_L versus *1/T*, ΔH of an adsorption process can be obtained (Equation 1.3).

$$Log\ K_L = \frac{-\Delta H}{2.303\mathrm{RT}} + \frac{\Delta S}{2.303\mathrm{R}} \tag{1.3}$$

Freundlich isotherm, which is presented by Freundlich in 1906 [105], can be written as follows

$$q_e = K_f C_e^{1/n} \tag{1.4}$$

where K_f is the Freundlich adsorption constant (mg/g), n is a dimensionless constant, q_e is the amount of metal adsorbed at equilibrium (mg/g) and C_e is the equilibrium concentration (ppm). The linear form of this equation is given as,

$$Log\ q_e = Log\ K_F + \frac{1}{n}\ LogC_e \qquad (1.5)$$

This model is applied to nonideal sorption on heterogeneous surfaces which explains multilayer sorption [101, 104]. Biosorbents are used to remove metal ions in an efficient manner. Most of the agricultural waste, which mainly contains cellulose and lignin, obeys the Langmuir adsorption isotherm [105]. Moreover, adsorption of heavy metals on natural substances, such as clay, peat and zeolites, has shown that almost all adsorbate-adsorbent interactions follow the Langmuir adsorption isotherm, suggesting monolayer adsorption [105].

Stephen Brunauer introduced the 1st classification on adsorption isotherms. This was later modified by IUPAC as colloidal and surface chemistry at 1985. Figure 1.11 represents the IUPAC classification of adsorption. According to this, there are six types of isotherms namely Type I, Type II, Type III, Type IV, Type V and Type VI.

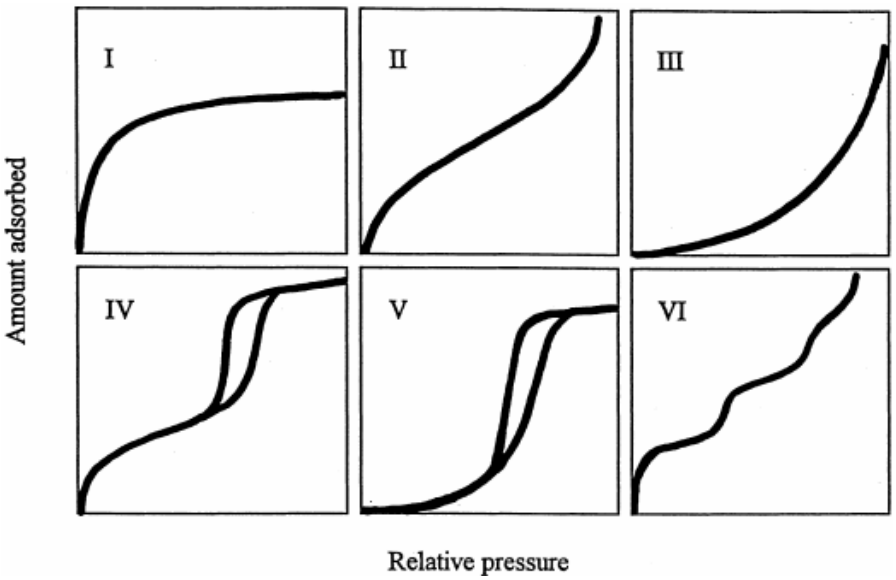

Figure 1.10: The IUPAC Classification of Adsorption Isotherms

Type I: Explain monolayer chemisorption and characterize as micro porous adsorbents, which have strong interactions between the adsorbate and adsorbent. (Ex: Molecule Sieve Zeolites, certain porous oxides, activated carbon types follow type I isotherm)

Type II: Indicates typical physical adsorption on nonporous or macroporous adsorbents with strong adsorbate – adsorbent interactions leading to a multi-layer adsorption.

Type III: Indicates physical adsorption on nonporous adsorbents with weak adsorbate – adsorbent interactions. The adsorbed molecules are clustered around the most favourable sites on the adsorbent surface.

Type IV: Occurs for strong adsorbate – adsorbent interactions when the material is mesoporous. It corresponds to systems involving capillary condensation in porous solids. Once the pores are filled, further adsorption to form multi-layer does not occur and results in a plateau region. Type IV, V show hysteresis because of capillary condensation.

Type V: Similar to Type III. This can be attributed to relatively weak adsorbate – adsorbent interactions. At higher concentrations / pressure, molecular clustering is followed by pore filling. (Ex: Water adsorption on hydrophobic microporous and mesoporous adsorbents)

Type VI: Represents a layer by layer adsorption on a highly uniform nonporous surface. The step height represents the capacity of each adsorbent layer and the sharpness of the step is dependent on the system and the temperature.

1.6.2 Kinetics Studies

Kinetics of an interested system has a great significance towards the adsorption in order to evaluate the performance of the adsorbent. Kinetics also provides an insight to the mechanism of the relative adsorption process. Further, kinetics data are useful for the design of wastewater treatment systems. Thus several adsorption kinetic models have been developed to explain the adsorption kinetics. Adsorption kinetics deals with the rate of a specific reaction. Hence, based on the rate of change of concentration of the reactants, several kinetic models are formulated such as first order, second order, pseudo first order, pseudo second order and reversible ones [106].

The earliest model of kinetics based on adsorption capacity was introduced by Lagergren. It can be shown as,

$$\frac{dq_t}{dt} = k'(q_e - q_t)^n \qquad (1.6)$$

where k' is the rate constant, t is contact time, q_e and q_t are amount of adsorbate adsorbed per unit weight of adsorbent at equilibrium and at time t, respectively, and n is the order of the reaction with respect to adsorbate. When the first order is considered, n equals to one. By integrating the above equation, pseudo first order equation can be obtained as follows:

$$ln(q_e - q_t) = -k't + lnq_e \qquad (1.7)$$

The pseudo second order kinetic equation can be found as,

$$\frac{t}{q_t} = \frac{1}{q_e}t + \frac{1}{(kq_e^2)} \qquad (1.8)$$

In most of the situations, where biosorbents are involved adsorption pseudo second order kinetic model was fitted well rather than the other kinetic models [107].

1.7 Objectives

The Objective of this research was to study the suitability of coconut coir / polyaniline composite as an adsorbent in order to remove Chromium (VI) from wastewater. Optimization of the experimental parameters to obtain highest efficiency of removal is always the initial step of adsorption experiments. The parameters optimized in this research were the shaking time, settling time and the initial pH of the metal solution.

However, to apply this model as a unit operation, good understanding of the characteristics of coconut coir / polyaniline composite and a thorough knowledge about Chromium (VI) ion interaction are needed. Further, adsorption

isotherm models, namely Langmuir and Freundlich, were studied to identify the type of adsorption, mechanism and to obtain an idea about the adsorbent. Finally, kinetic models were studied and the most suitable model for this experiment was found.

CHAPTER 2

MATERIALS AND METHODS

2.1 Materials

Coconut coir was obtained from Agricultural Research Institute, Gannoruwa, SriLanka. Analytical grade Aniline was distilled once at 182 - 184 °C temperature and stored at 4 °C until the experiment commenced. Potassium Persulphate was used as the oxidative agent of the polymerization. Standard solutions of Chromium (VI) were prepared using analytical grade Potassium dichromate. HNO_3 and NaOH solutions were used to prepare solutions of different initial pH values. Competitive adsorption experiments were carried out with standard solutions of heavy metal ions which were prepared by using analytical grade solutions. All the experiments were conducted under static conditions, with coconut coir particles of diameter (d) < 1.0 mm. Finally, PANI/CC composite was used to conduct X-ray fluorescence (XRF), Fourier transform infrared (FTIR) and scanning electron microscopic (SEM) experiments.

2.2 Instrumentation

The concentration of remaining chromium (VI) ions in solutions were measured using Spectro-Electronic M Series atomic absorption spectrophotometer (AAS). Concentrations of heavy metal ions in mixed solutions were measured using 4200 MP AES, Agilent technologies. XRF studies were carried out using Fischerscope Model-DF500FG-456 X-ray fluorescence spectrophotometer. FTIR spectra were studied on IR Prestige-21 (SHIMADZU) FTIR spectrophotometer. SEM images of samples were obtained from the ZEISS EVO|LS15 Scanning Electron Microscope.

2.3 Research Design

2.3.1 Preparation and Characterization of Coconut Coir / Polyaniline Composite

2.3.1.1 Sample Preparation

Emaraldine base form of polyaniline and coconut coir composite was prepared by chemical oxidation of Aniline in the presence of coconut coir as described below. Pre-cooled distilled Aniline (10 ml) was mixed with 0.1 mol dm^{-3} HCl (250 ml) and stirred in a 500 ml beaker. Potassium persulphate (15.00 g) was mixed with pre-cooled 0.1 mol dm^{-3} HCl (250 ml) and was stirred in an ice bath for few minutes until potassium persulphate dissolved completely. Then the solution was added to the aniline solution slowly which was stirred and kept in the ice bath. After that the solution was allowed to stir for additional 30 minutes. Then dried coconut coir (5.00 g) was added to the stirring solution slowly. Resulting solution was stirred for 2 hours and left overnight without stirring. Then PANI/CC composite was filtered dried in an oven and was stored in a desiccator until the experiment commenced.

2.3.1.2 XRF Analysis

XRF analysis was carried out by using PANI/CC composite samples and Cr(VI) treated PANI/CC composite samples. Cr(VI) adsorbed PANI/CC composite was obtained by stirring a suspension of PANI/CC composite in a solution of potassium dichromate and then filtering the suspension. Obtained samples of Cr(VI) adsorbed composite particles were air dried and used for XRF.

2.3.1.3 FTIR Analysis

Standard pellets were prepared by mixing (30:1 ratio) fused KBr with each powdered polyaniline, coconut coir and untreated composite samples respectively for Fourier Transform Infrared spectroscopic analysis.

2.3.1.4 SEM Analysis

Microscopic images of coconut coir and coconut coir / polyaniline composite samples were taken using Scanning Electron Microscope. They were used to investigate the surface morphology of the composite.

2.3.2 Competitive Adsorption Studies

Competitive adsorption experiment was carried out with zinc, cadmium, nickel, copper and chromium ions (Zn^{2+}, Cd^{2+}, Ni^{2+}, Cu^{2+}, $Cr_2O_7^{2-}$). A single mixture solution of 50 cm^3 volume was used with 10 mg L^{-1} of each ions and a dose of 0.50 g of PANI/CC composite. The pH of 5 was maintained. The shaking time and settling time was 60 minutes. Experiment was done in triplicate manner and remaining heavy metal concentrations were measured using 4200 MP AES. By using concentrations of heavy metal ions, adsorbed heavy metal percentages were found. Since Cr(VI) gives the best adsorption, research was focused on optimizing conditions for Cr(VI) adsorption.

2.3.3 Optimization of Experimental Parameters of Cr(VI) – PANI/CC Adsorption

Weighed masses of PANI/CC composite were added to 50.00 cm^3 of Cr(VI) solutions placed in small jars and pH values were measured. Each sample was shaken at (150 rpm speed) for a specified period of time and settled for a specified period of time. Next, the suspension was filtered. Finally, the filtrate concentration was measured using AAS. The percentage removal was calculated by using the following equation,

$$\text{Percentage removal} = \frac{C_i - C_f}{C_i} \times 100 \ \% \qquad (2.1)$$

where C_i is the initial concentration of the Cr(VI) in the solution before treatment and C_f is the final concentration of Cr(VI) in the filtrate after treatment. The concentrations C_i and C_f were determined with the help of a calibration curve constructed daily using standard solutions of Cr(VI) to improve the precision of measurements. All the experiments were carried out in triplicate, and average values were reported.

2.3.3.1 Optimization of Initial Solution pH

Effect of initial solution pH for the removal of Cr(VI) was studied at different pH values ranging from 1 to 6 with the use of 10 mg L^{-1} Cr(VI) solution. Solutions of different pH values were prepared using HNO_3 and/or NaOH. HNO_3 solution of

0.1 mol dm^{-3} and NaOH solution of 0.1 mol dm^{-3} were used to adjust the pH of initial Cr(VI) ion solutions to the desired value. Both the initial pH and the pH of each solution after treatment of Cr(VI) ion solutions with PANI/CC composite were checked. Experiment for optimization of initial solution pH was conducted at 0.10 g PANI/CC composite dosage, 60 min stirring time and 60 min settling time.

2.3.3.2 Optimization of PANI/CC Composite Dosage

Different masses of PANI/CC composite samples were weighed accurately ranging from 0.05 g to 1.00 g. Then 50.00 cm^3 samples of Cr(VI) with a concentration of 10 mg L^{-1} solutions were added to weighed composite samples placed in jars. Then the samples were stirred thoroughly at a speed of 150 rpm for 60 min followed by a constant settling time of 60 min. Throughout the experiment, the pH of initial Cr(VI) solutions was maintained at a value of 5.

2.3.3.3 Optimization of Stirring Time and Settling Time

50.00 cm^3 samples of 10.00 mg L^{-1} Cr(VI) solutions (pH $\approx$ 5.0) were separately stirred at a speed of 150 rpm with optimized dosage of PANI/CC composite for different stirring times ranging from 0 min to 60 min followed by a constant settling time of 60 min. After optimizing the shaking time, similar experiments were carried out to optimize settling time using the pre-determined optimum dosage and stirring time. Settling time was varied from 0 min to 60 min to determine the optimum value.

2.3.4 Isotherm Studies

Cr(VI) ion solutions of initial concentration varying from 10 mg L^{-1} to 600 mg L^{-1} were shaken with PANI/CC composite under optimized conditions of shaking time, settling time and pH. Each solution was then allowed to reach equilibrium, and the concentration of Cr(VI) ion in the supernatant solutions were measured. For each initial concentration, the same experimental procedure was followed in triplicate. The extent of adsorption was calculated as mass of Chromium adsorbed (in mg) on 1.00 mg of PANI/CC composite (mg mg^{-1}). A graph of the extent of adsorption versus initial Cr(VI) ion concentration was plotted.

Adsorption data were also analysed to check the validity of the Langmuir and Freundlich isotherms, and the isotherm constants of these models were calculated.

2.3.5 Kinetics studies

Kinetic experiments were carried out at ambient temperature (25 ºC) for further investigation of the interaction of Cr(VI) with PANI/CC composite. 1.00g of PANI/CC composite was treated with 980 cm^3 of 10 mg L^{-1} Cr(VI) solution and it was allowed to stir slowly with a magnetic stirrer. While the solution was being stirred, 5.00 cm^3 samples of the supernatant solution were withdrawn for a period of 104 min. The concentration of Cr(VI) in samples withdrawn was determined by AAS, and the extent of adsorption was calculated. By applying kinetic models for the data obtained in these experiments, the order of the reaction, such as first order, second order and pseudo second order was investigated.

2.3.6 Desorption studies

After completion of adsorption experiments with PANI/CC composite, Chromium (VI) adsorbed composite samples were washed with deionized water, and allowed to air-dry until a constant mass was obtained. Then, 0.50 g of Cr(VI) adsorbed composite sample was shaken with 50.0 cm^3 of pH-adjusted deionized water for 60 min and allowed to settle for 60 min. Then, concentration of Cr(VI) ion leached out was determined to calculate the extent of desorption. Desorption experiments were repeated for different initial pH values in the range of 1–10, adjusted with HNO_3 (0.1 mol dm^{-3}) and/or NaOH (0.1 mol dm^{-3}).

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Characterization of Coconut coir, Polyaniline and PANI/CC Composite

3.1.1 Bulk Characterization

Coconut coir consists of several organic substances having different functional groups which can be identified by FTIR. Further, if any metal-oxygen bonds are present, they can be identified using FTIR data. Generally, the adsorption capacities of adsorbents depend on chemical reactivity of these functional groups and the porosity [108].

FTIR spectra of coconut coir, polyaniline and PANI/CC composite indicates the presence of many functional groups (Figure 3.2). Since CC is a lignocellulose material, it showed broad absorption bands at 3340 cm^{-1} and 2922 cm^{-1} due to stretching vibrations of –OH and C-O. 1730 cm^{-1} and 1605 cm^{-1} due to C=O hemicellulose and lignin and 1240 cm^{-1} 1022 cm^{-1} due to C-O stretching of acetyl group of hemicellulose and plane deformation of aromatic C-H groups. PANI showed peaks at 1554 cm^{-1} and 1440 cm^{-1} due to stretching vibrations of the quinoid and benzenoid structures. PANI/CC composite shows most of characteristic peaks of PANI illustrating the complete coating of PANI on the surface of the composite.

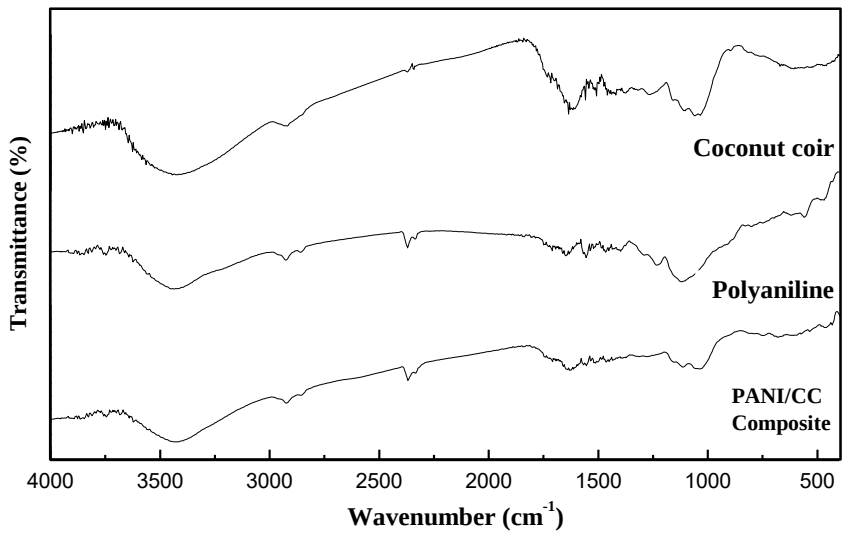

Figure 3.1: FTIR spectra of coconut coir, polyaniline and PANI/CC composite

XRF data provides information on metal contaminants, if any. According to the XRF patterns obtained, in addition to organic constituents present in coconut coir, metals such as Fe, Ca, Pb, Br, Sr, Zn and Cu are present at trace levels (Figure 3.1). This is supported by previous studies which indicate the presence of Cu, Zn, Fe, Mn, Mo and Ni in coir dust [109, 110].

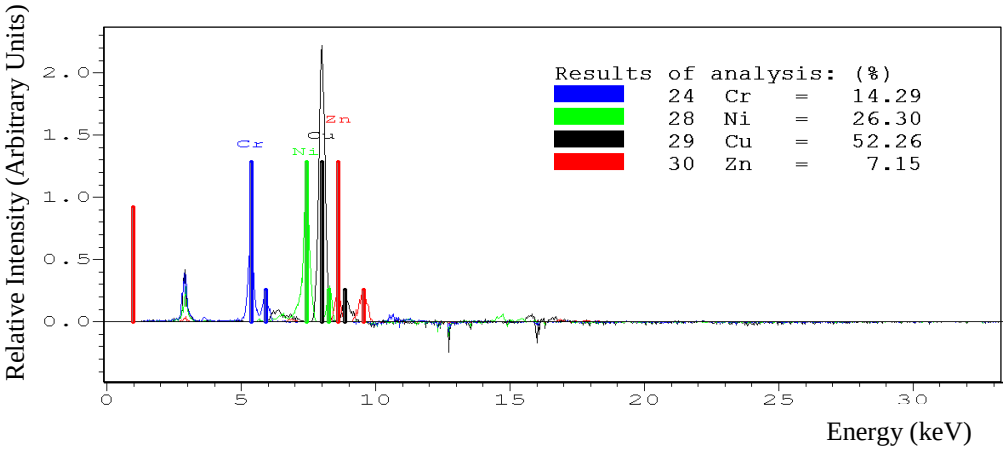

Figure 3.2: XRF analysis of coconut coir obtained from Gannoruwa agricultural research institute

Successful coating of PANI on CC surface that was evident by FTIR was further confirmed by SEM images. According to Figure 3.3 (a), CC has a porous structure with an average pore size of 20 µm of diameter. This porous structure of CC makes it a very good adsorbent material. Even after the coating with PANI, this porous structure remain intact as can be seen from Figure 3.3 (c). Further, upon coating with PANI, surface becomes smooth.

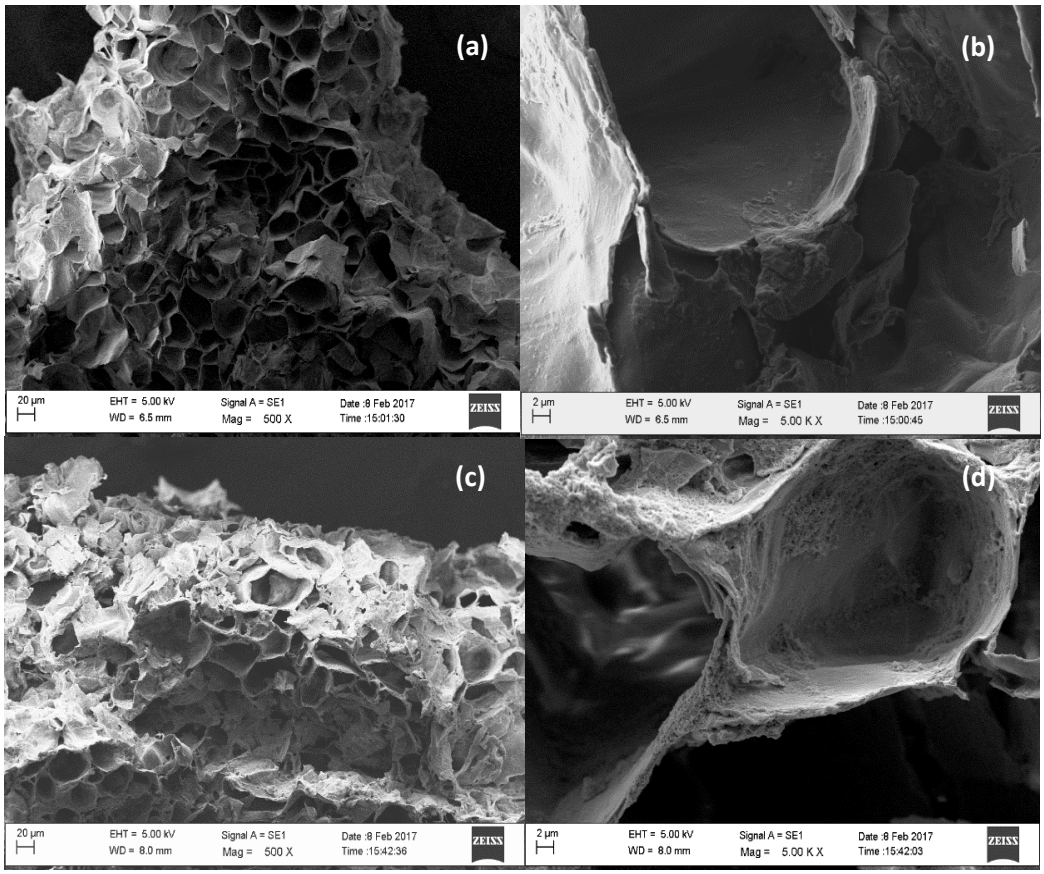

Figure 3.3: SEM Images of coconut coir (a) at 20 µm (b) at 2 µm and PANI/CC composite (c) at 20 µm, (d) at 2 µm

3.2 Competitive Adsorption Study with Common Heavy Metal Ions

In order to be a pragmatic application as an adsorbent, it is important that the composite work selectively with certain heavy metal ions. Therefore, a competitive adsorption experiment was carried out with zinc, cadmium, nickel, copper and chromium ions (Zn^{2+}, Cd^{2+}, Ni^{2+}, Cu^{2+}, $Cr_2O_7^{2-}$). A single mixture solution of 50 cm^3 volume was used with 10 mg L^{-1} of each ions and a dose of 0.5 g composite. The pH of 5 was maintained. The shaking time and settling time was 60 minutes. Experiment was done in triplicate manner. The results of the competitive experiment are summarized in Table 3.1.

Table 3.1: Competitive adsorption study results

	Zn^{2+}	Cd^{2+}	Cu^{2+}	Ni^{2+}	$Cr_2O_7^{2-}$
Initial Concentration (mg L^{-1})	12.69	12.77	12.98	14.97	10.37
Final Concentration (mg L^{-1})	12.62	12.69	12.13	14.05	6.84
Adsorbed Percentage	**< 1%**	**< 1%**	**7%**	**6%**	**34%**

According to Table 3.1, $Cr_2O_7^{2-}$ [Cr(VI)] showed the maximum adsorption yield. Therefore, research was focused on Cr(VI) removal and experimental conditions were optimized. In order to see whether the composite adsorb trivalent chromium [Cr(III)] pure Cr^{3+} solution was tested with the composite and it showed less than 5% adsorbed percentage. The small amounts of copper and nickel adsorption could be due to the non-uniform coating of PANI onto CC surface. Coconut coir surface has negatively induced charge by nature, which can interact with positive ions. These experimental data indicate that the PANI/CC composite is a selective adsorbent for Cr(VI) removal.

3.3 Optimization of Parameters that Affect the Removal of Cr(VI) by PANI/CC Composite

Removal of Cr(VI) using PANI/CC is an adsorption process which involves adsorbent-adsorbate interactions. Therefore, the extent of removal is expressed as percentage removal of the adsorbent by the adsorbate. The extent of removal of the adsorbent; in this case, the Cr(VI), depends on several experimental parameters, including initial solution pH, composite dosage, shaking time and settling time. If there are any pre-treatments that have been used in the preparation of the adsorbent, they also affect the extent of removal. The above mentioned parameters were optimized, one at a time, to obtain the maximum adsorption (or the maximum removal).

In order to optimize one parameter, that parameter was changed within an adequate range while keeping the other parameters constant. The removal percentage was calculated using Equation (2.1).

3.3.1 Effect of pH towards the Metal Adsorption

The pH of effluents is an important parameter that affects the removal of heavy metals. Further, the solubility or the ability of precipitation of metal ions depends on the pH of the effluent. Thus, adjustment of the pH of solution is very important in removing heavy metals from effluents. The extents of removal of Cr(VI) were determined at different pH values ranging from 1 to 6. For this experiment, $K_2Cr_2O_7$ solution with a concentration of 10 mg L^{-1} was used with a 0.10 g of PANI/CC composite dosage, 60 min shaking time and 60 min settling time. When pH is increased, the extent of Cr(VI) removal has fluctuated as shown in Figure 3.4.

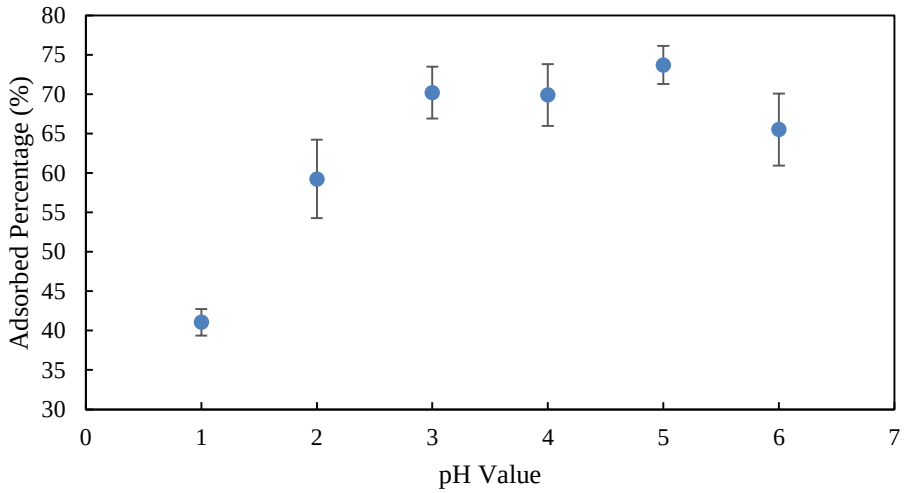

Figure 3.4: Percentage removal of $Cr_2O_7^{2-}$ by PANI/CC composite at different pH (60 min shaking time, 60 min settling time, 0.10 g composite mass, 10 mg L^{-1} $Cr_2O_7^{2-}$ 50.00 cm^3 solution)

Under acidic pH, the surface of polyaniline is high protonated. The protonated form of polyaniline can interact with dichromate anions by electrostatic attractions for high adsorption of Cr(VI). Optimum pH was concluded as pH 5. At pH 5, the surface of the PANI/CC is positively charged due to the protonation of Nitrogen atoms in amine groups. These positive charges make favorable electrostatic interactions with negatively charged Cr(VI) species resulting in higher percentage removal. Lower percentage removal before and after pH 5 could be explained as below. At pH values below 5, in very acidic conditions Cr(VI) can be easily reduced to Cr(III). Therefore, at high acidic conditions the adsorbed Cr(VI) on PANI/CC reduced to Cr(III) and there will be repulsive forces between

positively charged adsorbent surface and Cr(III), and releases Cr(III) to the solution. Since AAS gives total chromium, percentage removal is appeared to be increased. At pH values above 5 and specially in basic pH values deprotonation is dominating. Specially at high pH values, OH - may be adsorbed on the surface of PANI/CC through hydrogen bonds leading to negatively charged sites [111, 112]. The repulsion between negatively charged adsorbent surface and Cr(VI) result in lower percentage removal.

3.3.2 Effect of Adsorbent Dosage towards the Metal Adsorption

The PANI/CC composite dosage was varied from 0.05 to 1.00 g. Other experimental parameters were kept as pH of 5, shaking time of 60 min and settling time of 60 min. $K_2Cr_2O_7$ solution with a concentration of 10 mg L^{-1} was used for the experiment. Further, it was assumed that the temperature was constant during the entire time period of the experiment. Amount of adsorbed Cr(VI) was calculated form AAS data and adsorbed percentage at various dosage levels are shown in Figure 3.5.

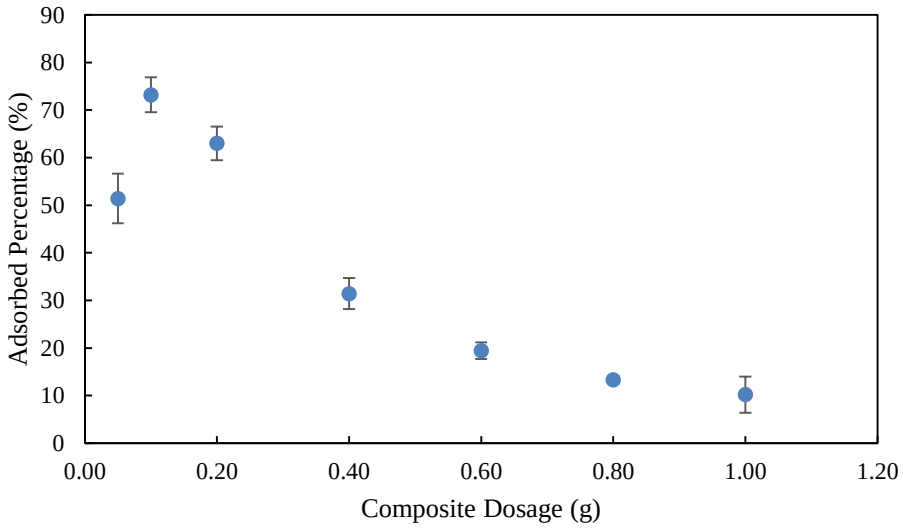

Figure 3.5: Percentage removal of $Cr_2O_7^{2-}$ by PANI/CC composite at different composite dosage (pH: 5, 60 min shaking time, 60 min settling time, 10 mg L^{-1} $Cr_2O_7^{2-}$ 50.00 cm^3 solution)

Composite dosage of 0.05 g is shown to be too low for the adsorption process and it could be due to the less adsorbent sites in surface for the adsorption process. The optimum dosage was found to be 0.10 g. During the experiment with high dosages of PANI/CC, higher the dosage; solution turned to color blue while shaking. The color blue arises due to the *Emaraldine Blue PANI* and PANI/CC

composite seems to be losing its binding property with PANI. It results PANI to disband from CC surface. Therefore, Cr(VI) ions get bound to PANI that had been mixed in the solution. After filtration, filtrate solution contains the majority of adsorbed chromium ions since PANI does not get filtered. The calculated adsorbed chromium percentage was found to be low because AAS measures overall chromium concentration in the solution.

3.3.3 Effect of Shaking Time towards the Metal Adsorption

Third parameter that was optimized was the shaking time. For this experiment, PANI/CC composite dosage of 0.10 g, $K_2Cr_2O_7$ solution with a concentration of 10 mg L^{-1} with a pH of 5 and settling time of 60 min were taken. Further, it was assumed that the temperature was constant during the entire experiment. The extent of removal of metal ions under investigation increases considerably during the initial one-hour period, beyond which they all show almost constant removal percentages (Figure 3.6).

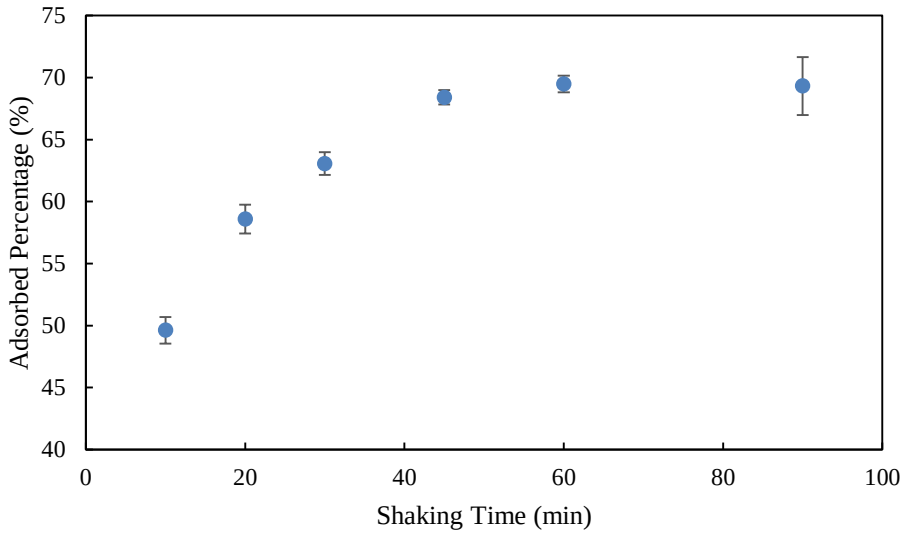

Figure 3.6: Percentage removal of $Cr_2O_7^{2-}$ by PANI/CC composite at different shaking time (0.10 g composite dosage, pH: 5, settling time 60 min, 10 mg L^{-1} $Cr_2O_7^{2-}$ 50.00 cm^3 solution)

At the beginning, more adsorption sites are available on PANI/CC surface for metal adsorption. Therefore, adsorbed percentage increases during the initial one-hour period. After a certain time, adsorption process comes to an equilibrium, therefore, it shows a constant removal percentage. The optimum shaking time was found to be 60 minutes.

3.3.4 Effect of Settling Time towards the Metal Adsorption

Settling time was optimized by using the optimum shaking time of 60 min. Other parameters were taken as PANI/CC composite dosage of 0.10 g and $K_2Cr_2O_7$ solution with a concentration of 10 mg L^{-1} with a pH of 5. It was experimentally determined that the removal percentage remained almost the same during the entire settling time period. Experimental data varied as followed (Figure 3.7).

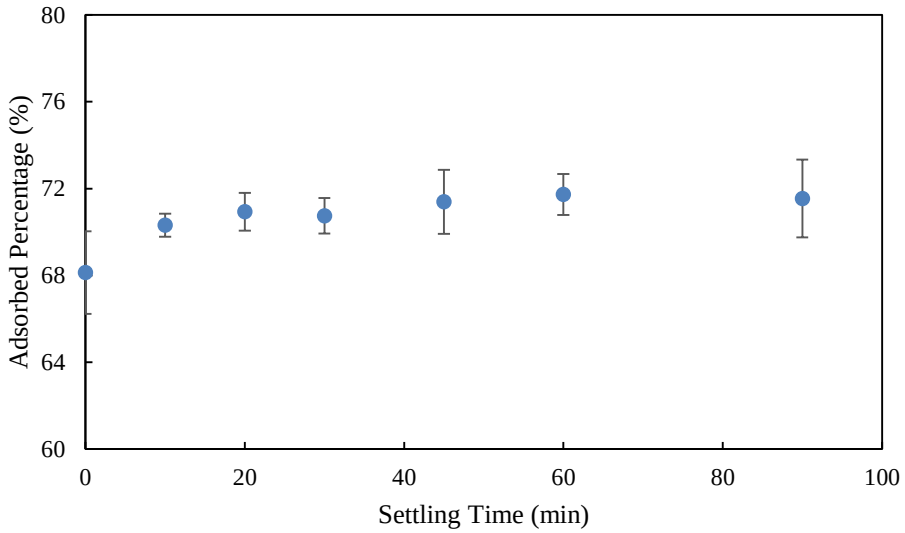

Figure 3.7: Percentage removal of $Cr_2O_7^{2-}$ by PANI/CC composite at different settling time (0.10 g composite dosage, 60 min shaking time, pH: 5, 10 mg L^{-1} $Cr_2O_7^{2-}$ 50.00 cm^3 solution)

Since this is an equilibrium process, it takes some time to reach the equilibrium. Therefore, at the initial stages of settling time a slight increment in adsorbed percentage was observed but after around 30-40 minutes, it became constant. To ensure that the equilibrium has reached, 60 minutes of settling time was selected as the optimum settling time.

3.3.5 Effect of Initial Cr(VI) Concentration towards the Metal Adsorption

The effect of initial Cr(VI) concentration towards the metal adsorption was tested by keeping all the other experimental conditions at optimized values. For this, 50 cm^3 of pure $K_2Cr_2O_7$ solutions were prepared with different concentrations ranging from 10 to 110 mg L^{-1}.

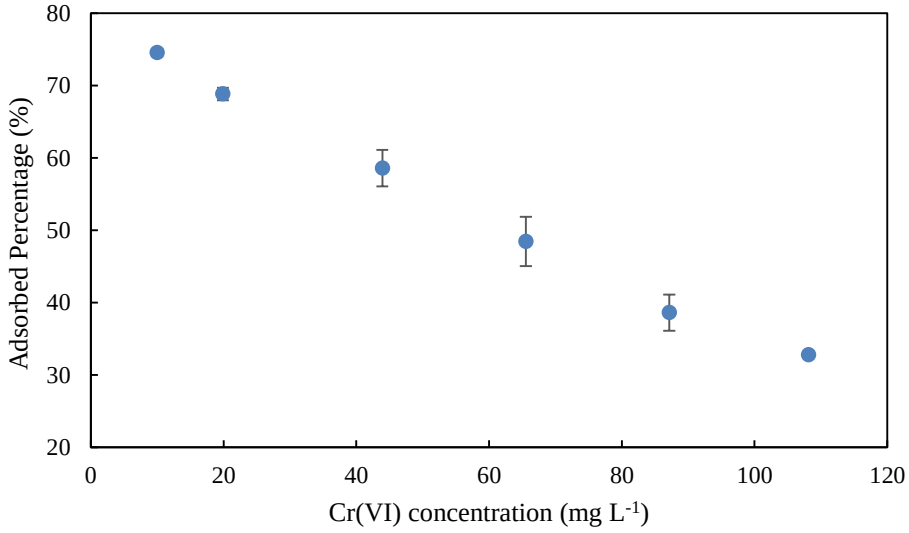

Figure 3.8: Percentage removal of $Cr_2O_7^{2-}$ by PANI/CC composite at different Cr(VI) concentration (pH: 5, 60 min shaking time, 60 min settling time, 0.10 g composite mass)

constant throughout the experiment since the composite dosage that was used kept constant. Therefore, a limited number of adsorption sites are available for the adsorption although the concentration of adsorbate increases. Furthermore, after all these sites being occupied, the adsorbent surface is almost coated with a layer of Cr(VI). This situation is called as a mono-layer formation and the binding nature is called as *chemisorption*. After forming a mono-layer, another layer could be bind on top of the mono layer due to various attractions. This situation is known as multi-layer formation and the binding is called as *physisorption*. In this study it was observed that Cr(VI) adsorbed on to PANI/CC systems through a multi-layer formation. More evidence for multi-layer formation is given and theoretically proved in the latter part of the section of adsorption isotherm.

3.4 Adsorption of Cr(VI) on PANI/CC Composite

When Cr(VI) and the PANI/CC (adsorbent) are in contact for a sufficient time period, an equilibrium is established between Cr(VI) ions in the solution and Cr(VI) ions adsorbed on the solid surface as shown below:

$$Cr_2O_7^{2-}\ (aq) \rightleftharpoons Cr_2O_7^{2-}\ (ads)$$

Adsorption of chromium onto PANI/CC composite was further proved qualitatively by XRF studies. XRF analysis was carried out with Cr(VI) adsorbed PANI/CC sample and as can be seen from Figure 3.9, there is a strong peak for chromium in XRF spectrum. By comparing with XRF analysis obtained before Cr(VI) treatment (Figure 3.2), it can be seen that a high amount of chromium had been adsorbed onto PANI/CC surface.

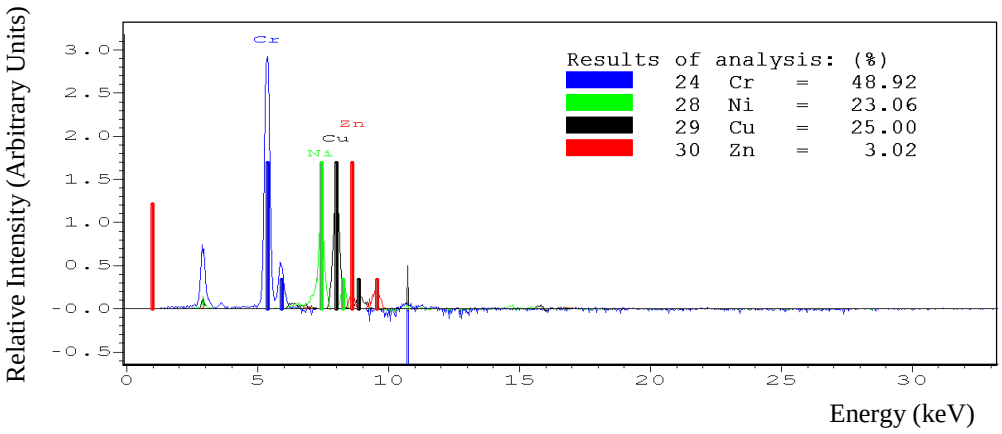

Figure 3.9: XRF plot of PANI/CC composite after treatment with $Cr_2O_7^{2-}$

Many equilibrium models exist to investigate the amount of metal ions sorbed by a certain adsorbent. The distribution of metal ions between the solution and the adsorbent at constant temperature can be expressed by isotherms. Adsorption isotherm is a relationship between the amount of adsorbate adsorbed by a unit mass of adsorbent and the activity of the adsorbate, which is expressed as the pressure or the concentration of the adsorbate, at constant temperatrue. Adsorption isotherms provide information about adsorption mechanism, surface properties and degree of affinity of adsorbents.

First classification on adsorption isotherms was introduced by Stephen Brunauer ,which later led to the modern classification of isotherms by IUPAC. IUPAC classification describes six types of isotherms, namely Type I, Type II, Type III, Type IV, Type V and Type VI. Each type has unique properties about the adsorbate - adsorbent interaction, and the classification depends on the shapes of the curves (Figure 1.1).

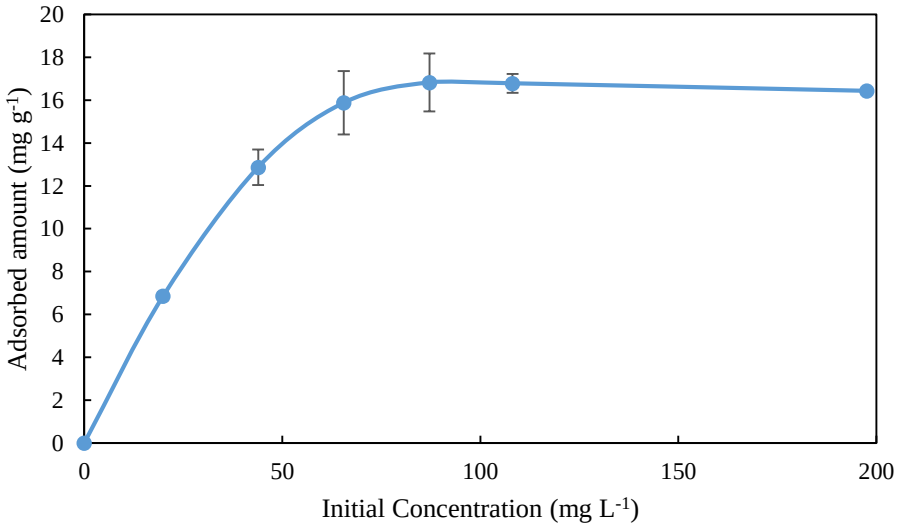

Figure 3.10: Equilibrium curve for the adsorption of Cr(VI) on PANI/CC as a function of initial concentration

The variation of the amount of Cr(VI) ion adsorbed on PANI/CC composite with respect to the initial concentration of Cr(VI) reflects *Type I* isotherm. This suggests that adsorbent is microporous where the pore size is not very much larger than that of the adsorbate [113].

Among various isotherm models, Langmuir and Freundlich models are widely used for investigation of metal ion-adsorbent systems [114, 115]. Hence these two isotherms were investigated in this research to study the behaviour of Cr(VI) and PANI/CC system. The Langmuir adsorption isotherm plotted according to Equation (1.2) is shown in Figure 3.12, while the linear form of Freundlich isotherm plotted according to Equation (1.4) is shown in Figure 3.13.

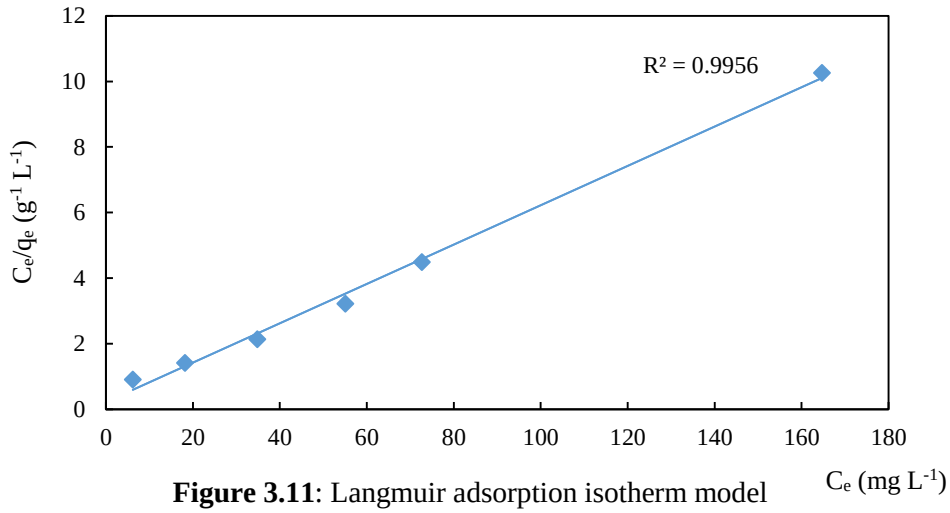

Figure 3.11: Langmuir adsorption isotherm model

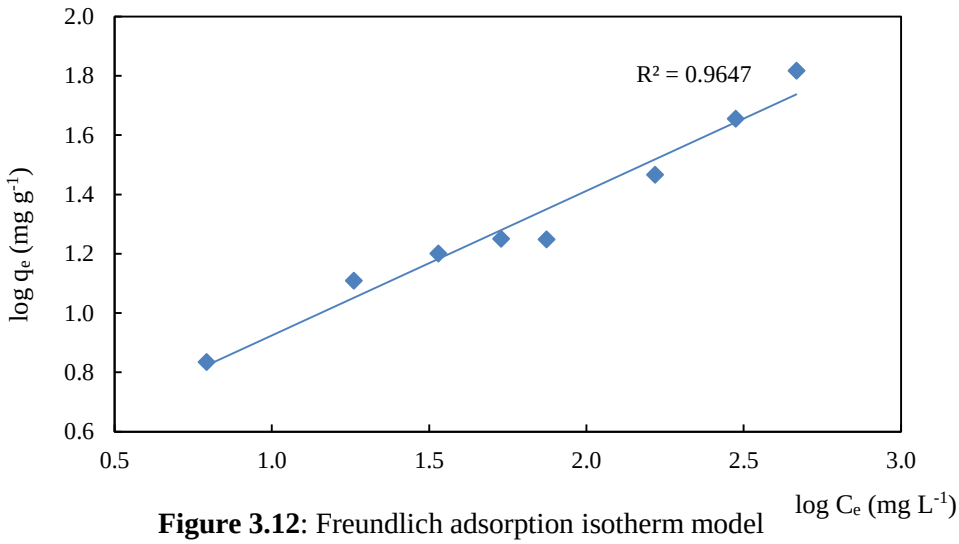

Figure 3.12: Freundlich adsorption isotherm model

The value of *n* in equation 1.4 can be calculated using the slope of the graph. If $n = 1$, then the partition of metal ions between the two phases is independent of concentration. If $n < 1$, it indicates a normal adsorption. If *n* lies between 1.0 and 10, it indicates a favourable sorption process. However, parameter *n* is a characteristic of a particular sorbent - sorbate system [116].

The accuracy of a selected isotherm model towards the experimental data was determined using the magnitude of linear regression coefficients, where by the isotherm which gives the R^2 value closest to unity was proven to be the best fit. When metal ion - adsorbent interactions are considered, it has shown to obey the Langmuir adsorption isotherm rather than the Freundlich isotherm, since the regression coefficients of Langmuir models are closer to 1.00 than that of the Freundlich isotherms (Table 3.3).

Table 3.3: Linear regression coefficient (R^2) values for each models

Metal ion	Langmuir model		Freundlich model	
	q_{max} (mg/g)	R^2	n	R^2
$Cr_2O_7^{2-}$	16.67	0.99	2.05	0.96

Since Cr(VI) ion – PANI/CC interactions follow the Langmuir isotherm model, it can be stated that the sorption occurs in a homogeneous way at the surface of the PANI/CC adsorbent and Cr(VI) forms a monolayer without having inter molecular interactions on the surface of the sorbent [101]. Cr(VI) is negatively charged and the surface of composite is positively charged. This situation easily leads to the formation of chemical bonds rather than physical bonds, so that metal ions are strongly attached to the surface forming a monolayer.

3.5 Kinetics Models of Adsorption of Cr(VI) on PANI/CC Composite

Kinetics studies and equilibrium studies play an important role in understanding adsorption systems. Adsorption processes involving a liquid phase and a solid phase would have multi-step reactions. This can be elaborated using kinetics studies. Kinetic studies related to adsorption processes are investigated using a constant amount of adsorbents. As the concentration of one reactant is kept constant, this type leads to pseudo order kinetics. In order to describe such systems, pseudo order models which describe how the rate depends on the equilibrium sorption capacity, but not on the concentration of the adsorbate were presented [117, 118]. Therefore, pseudo first order and pseudo second order equations were tested.

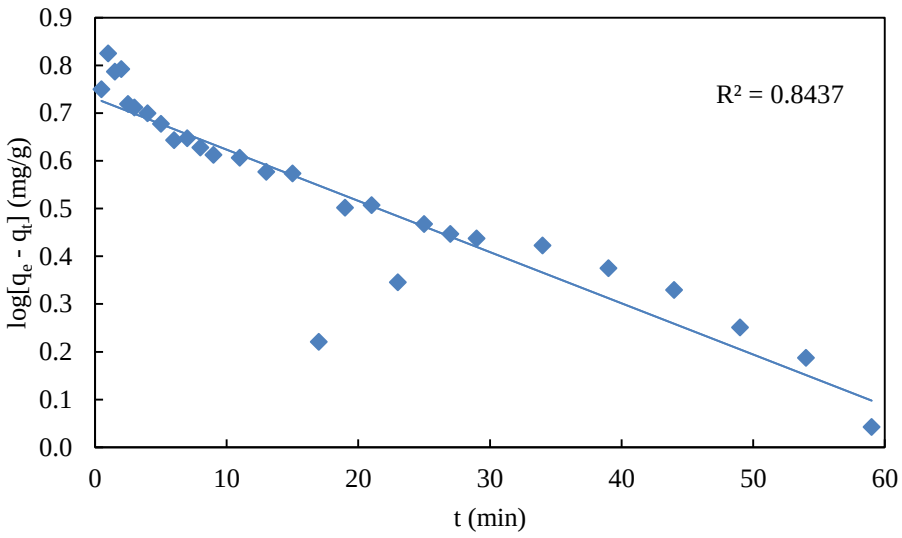

Figure 3.13: Pseudo first order calculation

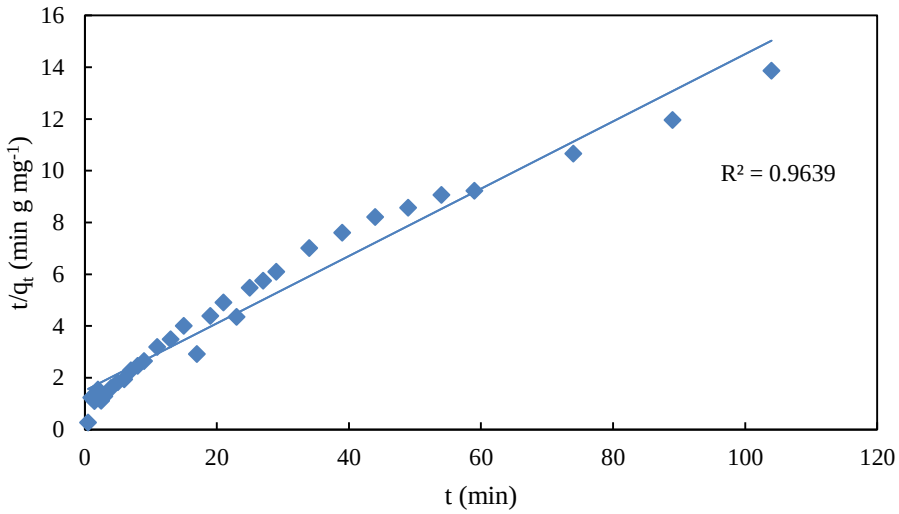

Figure 3.14: Pseudo second order calculation

According to Figure 3.14 and Figure 3.15 the highest R^2 value of 0.96 was observed for the *pseudo second order* model. Therefore, it was selected as the best suitable model for the adsorption process of Cr (VI) to PANI/CC composite. The assumption based on pseudo second order model is that the rate limiting step may be a chemisorption process where valence forces are involved through sharing or exchanging electrons between the sorbent and the sorbate (*i.e.*, chemisorption) [117].

3.6 Desorption Study of Cr(VI) on Treated PANI/CC Composite

Desorption of adsorbed Cr(VI) on PANI/CC is important when it comes to practical applicability where discarding or recycling these adsorbed composites are taking place. Desorption test was carried out in order to investigate this. For this study, first PANI/CC composite was treated with 10 mg L^{-1} $K_2Cr_2O_7$ solution by keeping other experimental parameters at their optimized values for adsorption. Then these treated composites were filtered and dried in air for overnight. After that, 0.5 g of dried composites were added to 50 cm^3 of deionized water having different pH values. The pH of solutions was optimized by using acid and base. After 60 min of shaking time and 60 min of settling time, desorbed chromium concentrations were determined by using AAS.

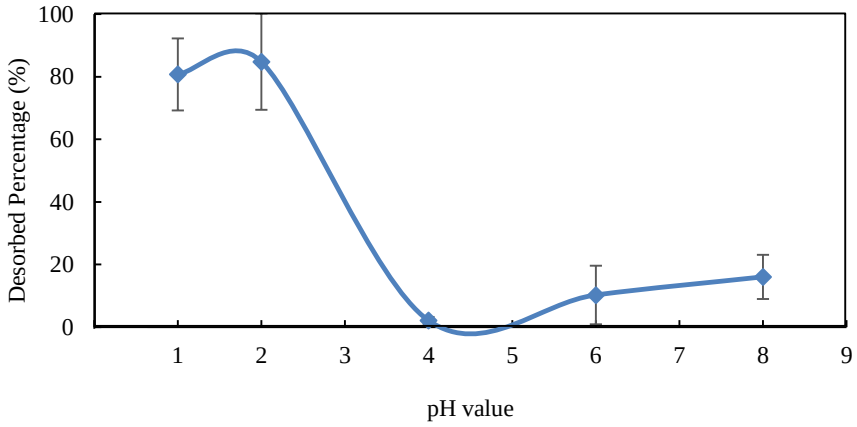

Figure 3.15: Desorption test results in relevance with different deionized pH valued water solutions

As shown in Figure 3.16 Cr(VI) desorption is highest in acidic pH region. Also desorption is relatively low in 6-8 pH range. In very acidic conditions adsorbed Cr(VI) on PANI/CC reduced to Cr(III) by PANI. These Cr(III) is repelled by positively charged N on protonated PANI. This could be the reason for the high desorption of chromium at pH 3.

Because of this pH dependency, adsorbed composites will not harm natural waterbodies by releasing chromium ions as this highly acidic conditions are not usual in natural waterbodies. Also, by maintaining pH 1-3 condition, chromium ions could be desorbed and could be used in relevant applications. This concludes

very well that the composite is pragmatic in adsorption and could be used in a good way after the composite is been treated.

CHAPTER 4

CONCLUSIONS AND FUTURE DIRECTIONS

According to FTIR analysis, CC contains functional groups; mainly carboxyllic groups, alcohol groups and hydroxyl groups which aids in metal removal. Coating the CC with Emarldine Base PANI increases the selectivity of metal adsorption particularly it becomes selective for Cr(VI) adsorption. This was evident by XRF and AES experimental data. FTIR and SEM analysis confirmed the successful formation of PANI/CC composite.

Optimization of experimental parameters leads to the highest Cr(VI) removal efficiency of 75%. The optimized conditions which were determined in this study are shown in Table 4.1.

Table 4.1: Optimized experimental parameters

Parameter	**Magnitude**
pH	5
Composite Dosage	0.10 g
Initial metal solution concentration	10 mg L^{-1}
Shaking time	60 min
Settling time	60 min

Moreover, the adsorption of $Cr_2O_7^{2-}$ on PANI/CC composite at low initial metal ion concentrations obeys Langmuir adsorption model and Type I IUPAC model. This unveils that monolayer formation is favoured and the adsorbent is microporous in nature. At higher concentrations, PANI/CC composite obeys freundlich adsorption model revealing the multi-layer adsorption property. The highest adsorption capacity on PANI/CC was found as 16.67 mg g^{-1}. Removal percentage is 75% for PANI/CC whereas pure PANI was reported to be 59.6% by Eisazadeh H [119]. Therefore, it can be said that this is an efficient, easily synthesized and inexpensive process to remove Cr(VI) selectively from waterbodies. Some of the already reported adsorbents and their adsorption capacities are summarized at Table 4.2. The newly synthesized PANI/CC

composite showed a better adsorption capacity when compared to the sorbent materials listed in Table 4.2. The interactions between ions and PANI/CC composite follows pseudo second order kinetics model which states that chemisorption has involved in the adsorption process.

Table 4.2: Summary of reported adsorption capacities for Cr(VI)

Sorbent Material	**Source**	**Adsorption Capacity (mg/g)**
Wollastonite-fly ash	Panday et al., 1984	0.271
Walnut Shell	Orhan and Büyükgüngör 1993	1.33
Waste Tea	Orhan and Büyükgüngör 1993	1.55
Turkish Cofee	Orhan and Büyükgüngör 1993	1.63
Sawdust	Bryant et al., 1992	10.1

Desorption governs only at highly acidic conditions and therefore, it will not harm natural waterbodies. At pH 1-2, 87% of chromium ions can be desorbed from Cr(VI) adsorbed PANI/CC composite in aqueous solutions. By considering all the above factors, it can be stated that PANI/CC is an effective adsorbent to remove Cr(VI) selectively from wastewater, which is both economically and environmentally friendly.

As a future projection, PANI/CC could be used with other adsorbents for an efficient heavy metal removal. Pure coconut coir surface is naturally negatively charged and it has been already tested for heavy metal adsorption. It has been already reported by other researchers that, among three metals, Pb^{2+} showed the highest adsorption capacity on CC which is 96.15 mg g^{-1} where as Zn^{2+} showed the lowest at 27.02 mg g^{-1} and Cu^{2+} showed a 33.7 mg g^{-1} adsorption [120]. After coating with PANI, PANI/CC adsorbed Cr(VI) and Cr(III) appears in solutions, which indicates that polyaniline is responsible for reduction of Cr(VI) to Cr(III) [121]. Therefore, by mixing PANI/CC with an adsorbent that adsorbs Cr(III), the efficiency of total chromium removal could be maximized.

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