REMOVAL OF TOXIC METAL IONS FROM INDUSTRIAL EFFLUENT USING BIO-ADSORBENT

Thesis submitted

By

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THESIS APPROVAL

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ABSTRACT

In the present work, the removal of metals ions such as Pb(II), Cd(II), Cr(III) from industrial effluent by batch adsorption technique using different bio-adsorbents were investigated. Standard solutions of the metal ions of different concentrations were prepared and their adsorption properties onto neem leaf powder (NLP), nut shell powder (NSP) and jute stick powder (JSP) were studied. The influence of initial metal ion concentration, contact time, pH, adsorbent dose, free energy and desorption studies were investigated. Experimental data for all the adsorbents were found to fit well to both Langmuir and Freundlich adsorption isotherm models. The experimental data revealed that these adsorbents are highly effective for the removal of Pb(II) and Cd(II) but a little bit less potential for the removal of Cr(III) from industrial effluents at pH 6-7. The data obtained were interpreted kinetically by using pseudo first order, and pseudo second order kinetic models. In all the cases, the adsorption kinetics followed pseudo second order rate equation.

NLP, NSP and JSP are very effective adsorbent for the removal of Pb(II), Cd(II) and Cr(III) even when their concentration is as low as 4 ppm. The main advantage of using NLP, NSP and JSP for the adsorptive removal of metal ions from wastewater lies in the fact that these adsorbents are most effective when the pH of the medium is about 6.5. So, NLP, NSP and JSP may be used as cost-effective and environment-friendly adsorbents for the removal and recovery of Pb(II), Cd(II) and Cr(III) ions from industrial wastewater.

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1. Introduction

1.1 Background

Over seventy percent of the earth's surface is covered with water and is vital for all known forms of life. Most of this water (about 97.5%) is in the oceans and seas and is too salty to drink or grow crops. Of the remaining 2.5%; 1.73% is frozen in the icecaps of Antarctica and Greenland leaving only about 0.77% available for our fresh water supply. Of the total water on the earth, only 0.0008% is available and renewable in rivers and lakes for human and agricultural use [1]. It is the water that falls as rain or snow or that has been accumulated and stored as groundwater that we depend on for our "clean" water resource. For 1.5 to 2.5 billion people in the world, clean water is a critical issue. It is estimated that by the year 2025, there will be an additional 2.5 billion people on the earth who will live in regions especially (Asia) Bangladesh already lacking sufficient clean water.

In many parts of the world, water is contaminated with sediments, nutrients, pathogens, dissolved oxygen, heavy metal ions, suspended solids, pesticides, turbidity, fish contamination and ammonia. Among these, prevalent contaminates in water are toxic metal ions. Metal ions are of serious concern as they are non-biodegradable and therefore persistent and as well as have the tendency to enter into the food chain through soil and waters [2].The increased exploration, production and consumption of the earth's raw materials (fossil fuels, minerals) coupled with rapid growth of the world's population over the past two hundred years have caused environmental accumulation of waste materials of which toxic metals like lead, cadmium, mercury, arsenic are prime suspects [3, 4]. Lead and cadmium are listed as major pollutants by United State Environmental Protection Agency with no chemical, biological or biochemical benefits to man, animals, plants and aquatic organisms [5, 6]. A variety of industries are responsible for the release of heavy metals into the environment through wastewater [7]. It is difficult and expensive to clean these pollutants/contaminants especially when the concentrations are relatively low. They are problematic, due to their persistence in the environment and potential toxic effect on ecosystem and human health. Concern related to these contaminants is particularly pertinent in Asia where the pollution with metal ions has been increasing dramatically due to changing agricultural practices and rapidly expanding industrialization.

The accumulation of heavy metal ions in the environment has become a serious concern due to growing risks to public health. These contaminants, such as cadmium, enter the environment through industrial waste; mill tailings, tanneries and land fill runoff. Exposure to heavy metal contamination has been found to cause kidney damage and anemia in low doses and in high concentrations, heavy metals can be carcinogenic and teratogenic if not fatal [8]. Several episodes due to heavy metal contamination in aquatic environment increased the awareness about the heavy metal toxicity. Among these, Minamata tragedy due to mercury poisoning and "Itai-Itai" disease in Japan due to cadmium toxicity are well known.

Precipitation, ion exchange, electrochemical processes and membrane filtration processes are commonly applied to the treatment of industrial effluents. However, the application of such processes is often restricted because of technical or economic constraints [9-10]. Developing cost effective and environmental friendly technologies for the remediation of wastewaters polluted with toxic substances is a topic of global interest.

Recently, a new scientific area has been developed that could help to recover heavy metals: the biosorption method. Biosorption is a process that utilizes inexpensive dead biomass to sequester toxic heavy metals and is particularly useful for the removal of contaminants from industrial effluents [11]. Bio-sorption of heavy metals is one of the most promising technologies involved in the removal of toxic metals from industrial waste streams and natural waters. There has been a tremendous amount of attention given to the use of biological systems for removal of heavy metal ions from the contaminated areas [12-17]. These new separation methods are effective and environmentally acceptable at affordable cost [18]. It is a potential alternative to conventional processes for the removal of metals. One of the pioneer reports, concerning biosorption has described the way abundant biological materials could be used to remove, at very low cost, even small amounts of toxic heavy metals from industrial effluents. Metal-sequestering properties of dead biomass provide a basis for a new approach to remove heavy metals when they occur at low concentrations [19].

More recently, phytoremediation has emerged as one of the alternative technologies for removing pollutants from the environment. Interest in using plants for environmental remediation is increasing due to their natural capacity to accumulate heavy metals and degrade organic compounds [20-22]. Since chemical functional groups are most likely responsible for metal binding, it is likely that higher plant cells might also be capable of binding metal ions.

Availability is a major factor to be taken into account in selecting biomass for clean-up purposes. The economy of environmental remediation dictates that the biomass must come from nature or even has to be a waste material. Seaweeds, molds, yeasts, bacteria, crabshells, among other kinds of biomass, have been tested for metal biosorption with very encouraging results. Cost effectiveness is the main attraction of metal biosorption, and it should be kept that way. Not only should microbial biomass be used directly, but biosorbent derived from it in a simple process should be the most low-priced for economical metal-removal process applications.

1. 2 Toxic Metal Ions

Today mankind is exposed to the highest levels in recorded history of lead, mercury, arsenic, aluminum, copper, nickel, tin, antimony, bromine, bismuth and vanadium pollution. Levels are up to several thousand times higher than in primitive man. Toxic metals are also persistent and cumulative. Late Dr. Henry Schroeder, MD, who was a world authority on trace elements, wrote: “Most organic substances are degradable by natural processes. (However), no metal is degradable; they are here to stay for a long time”.

Toxic metals replace nutrient minerals in enzyme binding sites. When this occurs, the metals inhibit, over stimulate or otherwise alter thousands of enzymes. An affected enzyme may operate at 5% of normal activity. This may contribute to many health conditions. Toxic metals may also replace other substances in other tissue structures. These tissues, such as the arteries, joints, bones and muscles, are weakened by the replacement process.

Toxic metals may also simply deposit in many sites, causing local irritation and other toxic effects. They may also support development of fungal, bacterial and viral infections that are difficult or impossible to eradicate until this cause is removed.

The mineral replacement process often involves the idea of preferred minerals. For example, the body prefers zinc for over 50 critical enzymes. However, if zinc becomes deficient - and our soil and food are very low in zinc today - or exposure to cadmium, lead or mercury is sufficiently high, the body will use these in place of zinc.

Cadmium, in particular, is located just below zinc in the periodic table of the elements, so its atomic structure is very similar to that of zinc. It almost fits perfectly in the zinc binding sites of critical enzymes such as RNA transferase, carboxypeptidase, alcohol dehydrogenase and many others or great importance in the body.

The ability to replace a vital mineral means, however, that toxic metals are not completely harmful. Indeed, they can extend life. They keep bodies functioning when vital minerals are deficient.

An analogy is to imagine taking an automobile journey. If one is far away from a repair shop when a key part like the fan belt breaks, if one had a spare piece of rope, one could tie it around the pulleys and continue the trip slowly.

The rope would not function nearly as well as the original part, but would allow one to keep going. This is how toxic metals can function positively in the body. Many people limp along on grossly deficient diets, and are even born deficient and toxic.

They do not realize their fatigue and other symptoms are due to the presence of incorrect “replacement parts” in their biological engine compartments. Depending on where toxic metals accumulate, the resulting effects may be given names such as hypothyroidism, diabetes or cancer.

Toxic Metals and Human Health

Toxic metals, including "heavy metals," are individual metals and metal compounds that negatively affect people's health. Toxic metals comprise a group of minerals that have no known function in the body and, in fact, are harmful. Today mankind is exposed to the highest levels of these metals in recorded history.

This is due to their industrial use, the unrestricted burning of coal, natural gas and petroleum, and incineration of waste materials worldwide. Toxic metals are now everywhere and affect everyone on the earth. They have become a major cause of illness, aging and even genetic defects. The toxicity of metals most commonly involves the brain and the kidney, but other manifestations occur, and some metals, such as arsenic, are clearly capable of causing cancer. An individual with metals toxicity, even if high dose and acute, typically has very general symptoms, such as weakness or headache. This makes the diagnosis of metals toxicity in a clinical setting very difficult unless a clinician has the knowledge and training to suspect the diagnosis and is able to order the correct diagnostic test. Chronic exposure to metals at a high enough level to cause chronic toxicity effects (such as hypertension in individuals exposed to lead and renal toxicity in individuals exposed to cadmium) can also occur in individuals who have no symptoms.

Basic Reference Guide to the Sources and Symptoms of the Common Toxic Metals:

Sources

Arsenic - pesticides, beer, table salt, tap water, paints, pigments, cosmetics, glass and mirror manufacture, fungicides, insecticides, treated wood and contaminated food.

Cadmium - cigarettes, (tobacco and marijuana), processed and refined foods, large fish, shellfish, tap water, auto exhaust, plated containers, electroplating, motor oil, galvanized pipes, air pollution from incineration and occupational exposure.

Copper - tap water, pesticides, swimming in pools, intra-uterine devices, vegetarian diets, dental amalgams, nutritional supplements - especially prenatal vitamins, birth control pills, weak adrenal glands and occupational exposure.

Lead - tap water, cigarette smoke, hair dyes, paints, inks, pencils, glazes, pesticide residues and occupational exposure in battery manufacture and other industries.

Mercury - dental amalgams, large fish, shellfish, medications, air pollution, manufacture of paper, chlorine, adhesives, fabric softeners and waxes.

Chromium - steel alloys, bricks in furnaces, dyes and pigments, plating, leather tanning, and wood preserving.

Nickel - hydrogenated oils (margarine, commercial peanut butter and shortening), shellfish, air pollution, cigarette smoke, plating and occupational exposure.

Symptoms

Arsenic - abdominal pain, abnormal ECG, anorexia, dermatitis, diarrhea, edema, enzyme inhibitor, fever, fluid loss, goiter, hair loss, headache, herpes, impaired healing, interferes with the uptake of folic acid, inhibition of sulfhydryl enzyme systems, jaundice, keratosis, kidney and liver damage, muscle spasms, pallor, peripheral neuritis, sore throat, stomatitis, stupor, vasodilation, vertigo, vitiligo and weakness.

Cadmium - hypertension, arthritis, diabetes, anemia, arteriosclerosis, impaired bone healing, cancer, cardiovascular disease, cirrhosis, reduced fertility, hyperlipidemia, hypoglycemia, headaches, osteoporosis, kidney disease, schizophrenia and strokes.

Copper - acne, adrenal hyperactivity and insufficiency, agoraphobia, allergies, hair loss, anemia, anxiety, arthritis, autism, cancer, chronic candida albicans infection, depression, elevated cholesterol, cystic fibrosis, depression, diabetes, dyslexia, elevated estrogen, failure to thrive, fatigue, fears, fractures of the bones, headaches, heart attacks, hyperactivity, hypertension, hypothyroidism, infections, inflammation, insomnia, iron storage diseases, kidney and liver dysfunctions, decreased libido, multiple sclerosis, nervousness, osteoporosis, panic attacks, premenstrual syndrome, schizophrenia, strokes, tooth decay and vitamin C and other vitamin deficiencies.

Lead - abdominal pain, adrenal insufficiency, anemia, arthritis, arteriosclerosis, attention deficit, back problems, blindness, cancer, constipation, convulsions, deafness, depression, diabetes, dyslexia, epilepsy, fatigue, gout, impaired glycogen storage, hallucinations, hyperactivity, impotency, infertility, inflammation, kidney dysfunction, learning disabilities, diminished libido, migraine headaches, multiple sclerosis, psychosis, thyroid imbalances and tooth decay.

Mercury - adrenal gland dysfunction, alopecia, anorexia, ataxia, bipolar disorder, birth defects, blushing, depression, dermatitis, discouragement, dizziness, fatigue, headaches, hearing loss, hyperactivity, immune system dysfunction, insomnia, kidney damage, loss of self-control, memory loss, mood swings, nervousness, numbness and tingling, pain in limbs, rashes, excessive salivation, schizophrenia, thyroid dysfunction, timidity, tremors, peripheral vision loss and muscle weakness.

Chromium - epigastric pain, nausea, vomiting, severe diarrhea, corrosion of skin, respiratory tract, lungs carcinoma, ulcers, convulsions, kidney and liver damage.

Nickel - cancer (oral and intestinal), depression, heart attacks, hemorrhages, kidney dysfunction, low blood pressure, malaise, muscle tremors and paralysis, nausea, skin problems, tetany and vomiting.

1.2.1 Lead

Lead is a main-group element in the carbon group with the symbol Pb (from Latin: *plumbum*) and atomic number 82. Lead is a soft, malleable poor metal. It is also counted as one of the heavy metals. Metallic lead has a bluish-white color after being freshly cut, but it soon tarnishes to a dull grayish color when exposed to air. Lead has a shiny chrome-silver luster when it is melted into a liquid.

Lead is used in building construction, lead-acid batteries, bullets and shots, weights, as part of solders, pewter's, fusible alloys and as a radiation shield. Lead has the highest atomic number of all of the stable elements, although the next higher element, bismuth, has a half-life that is so long (much longer than the age of the universe) that it can be considered stable. Its four stable isotopes have 82 protons, a magic number in the nuclear shell model of atomic nuclei.

Lead, at certain exposure levels, is a poisonous substance to animals as well as for human beings. It damages the nervous system and causes brain disorders. Excessive lead also causes blood disorders in mammals. Like the element mercury, another heavy metal, lead is a neurotoxin that accumulates both in soft tissues and the bones. Lead poisoning has been documented from ancient Rome, ancient Greece, and ancient China.

Lead is bright and silvery when freshly cut but the surface rapidly tarnishes in air to produce the commonly observed dull luster normally associated with lead. It is a dense, ductile, very soft, highly malleable, bluish-white metal that has poor electrical conductivity when compared to most other metals. This metal is highly resistant to corrosion, and because of this property, it is used to contain corrosive liquids (for example, sulfuric acid). Because lead is very malleable and resistant to corrosion it is extensively used in building construction – for example in the external coverings of roofing joints.

Metallic lead can be toughened by addition of small amounts of antimony, or a small number of other metals such as calcium. All isotopes of lead, except for lead-204, can be found in the end products of the radioactive decay of the even heavier elements, uranium and thorium.

Powdered lead burns with a bluish-white flame. As with many metals, finely divided powdered lead exhibits pyrophoricity. Toxic fumes are released when lead is burned.

Lead is a naturally occurring bluish-gray metal found in small amounts in the earth’s crust. It has no special taste or smell. It can be found in all parts of our environment. Most of it came from human activities like mining, manufacturing, and the burning of fossil fuels. Lead is used as a construction material for equipment used in sulfuric acid manufacture, petrol refining, halogenation, sulfonation, extraction and condensation. It is used in storage batteries, alloys, solder, ceramics and plastics. It is also used in the manufacture of pigments, tetraethyl lead and other lead compounds, in ammunition, and for atomic radiation and x-ray protection. Lead is used in aircraft manufacture, building construction materials (alloyed with copper, zinc, magnesium, manganese and silicon), insulated cables and wiring, household utensils, laboratory equipment, packaging materials, reflectors, paper industry, printing inks, glass industry, water purification and waterproofing in the textile industry.

Isotopes

Lead can be found or produced in many isotopes, with three of them being stable. The four natural isotopes of lead are ^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb with the slightly radioactive ^{204}Pb regarded as completely primordial lead, and the stable isotopes 206, 207, 208 being formed probably from the radioactive decay of two isotopes of uranium (U-235 and U-238) and one isotope of thorium (Th -232).

The one common radiogenic isotope of lead, ^{202}Pb, has a half-life of about 53,000 years.

Chemistry

Various oxidized forms of lead are easily reduced to the metal. An example is heating PbO with mild organic reducing agents such as glucose. A mixture of the oxide and the sulfide heated together will also form the metal.

$$2PbO + PbS \rightarrow 3Pb + SO_2$$

Metallic lead is attacked (oxidized) only superficially by air, forming a thin layer of lead oxide that protects it from further oxidation. The metal is not attacked by sulfuric or hydrochloric acids. It dissolves in nitric acid with the evolution of nitric oxide gas to form dissolved $Pb(NO_3)_2$.

$$3Pb + 8H^+ + 8NO_3^- \rightarrow 3Pb^{2+} + 6NO_3^- + 2NO + 4H_2O$$

When heated with nitrates of alkali metals, metallic lead oxidizes to form PbO (also known as litharge), leaving the corresponding alkali nitrite. PbO is representative of lead's +2 oxidation state. It is soluble in nitric and acetic acids, from which solutions it is possible to precipitate halide, sulfate, chromate, carbonate ($PbCO_3$), and basic carbonate ($Pb_3(OH)_2(CO_3)_2$) salts of lead. The sulfide can also be precipitated from acetate solutions. These salts are all poorly soluble in water. Among the halides, the iodide is less soluble than the bromide, which, in turn, is less soluble than the chloride.

Lead(II) oxide is also soluble in alkali hydroxide solutions to form the corresponding plumbite salt.

$$PbO + 2OH^- + H_2O \rightarrow Pb(OH)_4^{2-}$$

Chlorination of plumbite solutions causes the formation of lead's +4 oxidation state.

$$Pb(OH)_4^{2-} + Cl_2 \rightarrow PbO_2 + 2Cl^- + 2H_2O$$

Lead dioxide is representative of the +4 oxidation state, and is a powerful oxidizing agent. The chloride of this oxidation state is formed only with difficulty and decomposes readily into lead(II) chloride and chlorine gas. The bromide and iodide of lead(IV) are not known to exist. Lead dioxide dissolves in alkali hydroxide solutions to form the corresponding plumbates.

$$PbO_2 + 2OH^- + 2H_2O \rightarrow Pb(OH)_6^{2-}$$

Lead also has an oxide with mixed +2 and +4 oxidation states, red lead (Pb_3O_4), also known as minium.

Lead (II) forms a series of complexes with chloride, the formation of which alters the corrosion chemistry of the lead. This will tend to limit the solubility of lead in saline media.

Equilibrium constants for aqueous lead chloride complexes at 25 °C

$Pb^{2+} + Cl^{-} \rightarrow PbCl^{+}$ $K_1 = 12.59$

$PbCl^{+} + Cl^{-} \rightarrow PbCl_2$ $K_2 = 14.45$

$PbCl_2 + Cl^{-} \rightarrow PbCl_3^{-}$ $K_3 = 3.98 \times 10-1$

$PbCl_3^{-} + Cl^{-} \rightarrow PbCl_4^{2-}$ $K_4 = 8.92 \times 10-2$

The anaemia of lead poisoning is usually thought to be normochromic and normocytic, and punctate basophilia is regarded as a constant feature of the well–developed case.Formerly the anaemia in lead poisoning was attributed to a shortened survival of cells in the circulation but more recently the importance of interference with haemoglobin synthesis has been recognized. More than one mechanism has been blamed for the production of the anaemia of lead poisoning. The red cells may be rendered more ‘brittle’ by the lead and therefore may have a shorter life span than normal.

Lead as an Environmental Pollutant

1) Lead was used extensively as a corrosion inhibitor and pigment in both interior and exterior oil-based paints prior to 1978, and some paints were manufactured with lead concentrations of 50 percent by weight [23]. Therefore, weathering of lead-based exterior paint and deposition of paint chips and dust on soils remains a significant source of lead to soils surrounding homes. Lead concentration in soil at or above 500 micrograms per gram will result in a 1 to 5 percent probability that a child will have a blood lead concentration that equals or exceeds 10 micrograms per deciliter.

2) Drinking water is another source of ingested lead. Household plumbing fixtures, including metal pipes, faucets, and soldered joints, are possible sources of lead in

drinking water. The lower the pH of the water and the lower the concentration of dissolved salts in the water, the greater is the solubility of lead in the water. Leaching of lead from plastic pipes has also been documented and has been attributed to the use of lead stearate, a stabilizer used in the manufacture of polyvinyl plastics.

Lead is a Dangerous Source of Environmental Pollutant

Children are more at risk to lead poising because their bodies are in a continuous state development. Lead is absorbed at a faster rate by children compaired to adults. The primary cause of lead poisoning is its interference with a variety of enzymes because it binds to sulfahydryl groups found in a many enzymes. Part of lead poisoning results from its ability to mimic other metal ions that take part in biological progresses.

H. W. Mielke [24] suggest that effective prevention assumes an accurate identification of the environmental reservoirs of lead, and that current policies to reduce lead exposure are based on the assumption that the greatest lead hazard comes from lead-based paints. Most lead-based have now been removed from the market, and parents have been instructed to guard their children from eating paint flakes. However, for children, paint is now neither the most abundant nor the most accessible source of lead. The common problem is lead dust in the environment, with the soil a giant reservoir of tiny particles of lead. The greatest risk for exposure of inner city children is in the yards around houses and to a lesser extent in public playgrounds.

The author suggests that an accurate and complete appreciation of the distribution of lead in the environment can help shape policies that more effectively protect the health of children. The author concludes: "It took nearly 10 decades for lead to accumulate to its current levels in urban areas. With judicious planning, the problem can be resolved in much less time."

1. 2. 2. Cadmium

Cadmium is a chemical element with the symbol Cd and atomic number 48. This soft, bluish-white metal is chemically similar to the two other stable metals in group 12, zinc and mercury. Similar to zinc, it prefers oxidation state +2 in most of its compounds and similar to mercury it shows a low melting point compared to transition metals. Cadmium and its congeners are not always considered transition metals, in that they do not have partly filled d or f electron shells in the elemental or common oxidation states. The average concentration of cadmium in the Earth's crust is between 0.1 and 0.5 parts per million (ppm). It was discovered in 1817 simultaneously by Stromeyer and Hermann, both in Germany, as an impurity in zinc carbonate.

Cadmium occurs as a minor component in most zinc ores and therefore is a byproduct of zinc production. It was used for a long time as a pigment and for corrosion resistant plating on steel while cadmium compounds were used to stabilize plastic. With the exception of its use in nickel–cadmium batteries and cadmium telluride solar panels, the use of cadmium is generally decreasing in its other applications. These declines have been due to competing technologies, cadmium’s toxicity in certain forms and concentration and resulting regulations [25]. Although cadmium has no known biological function in higher organisms, a cadmium-dependent carbonic anhydrase has been found in marine diatoms

Cadmium is a soft, malleable, ductile, bluish-white divalent metal. It is similar in many respects to zinc but forms complex compounds. Unlike other metals, cadmium is resistant to corrosion and as a result it is used as a protective layer when deposited on other metals. As a bulk metal, cadmium is insoluble in water and is not flammable; however, in its powdered form it may burn and release toxic fumes [26].

Although cadmium usually has an oxidation state of +2, it also exists in the +1 state. Cadmium and its congeners are not always considered transition metals, in that they do not have partly filled d or f electron shells in the elemental or common oxidation states.[5] Cadmium burns in air to form brown amorphous cadmium oxide (CdO); the crystalline form of this compound is a dark red which changes color when heated, similar to zinc oxide. Hydrochloric acid, sulfuric acid and nitric acid dissolve cadmium by forming cadmium chloride ($CdCl_2$), cadmium sulfate ($CdSO_4$), or cadmium nitrate ($Cd(NO_3)_2$). The oxidation state +1 can be reached by dissolving cadmium in a mixture of cadmium chloride and aluminium chloride, forming the Cd_2^{2+} cation, which is similar to the Hg_2^{2+} cation in mercury(I) chloride.

$$Cd + CdCl_2 + 2AlCl_3 \rightarrow Cd_2[AlCl_4]_2$$

Isotopes

Naturally occurring cadmium is composed of 8 isotopes. Two of them are naturally radioactive, and three are expected to decay but have not been experimentally confirmed to do so. The two natural radioactive isotopes are ^{113}Cd (beta decay, half-life is 7.7×10^{15} years) and ^{116}Cd (two-neutrino double beta decay, half-life is 2.9×10^{19} years). The other three are ^{106}Cd, ^{108}Cd (both double electron capture), and ^{114}Cd (double beta decay); only lower limits on their half-life times have been set. At least three isotopes – ^{110}Cd, ^{111}Cd, and ^{112}Cd – are stable. Among the isotopes that do not occur naturally, the most long-lived are ^{109}Cd with a half-life of 462.6 days, and ^{115}Cd with a half-life of 53.46 hours. All of the remaining radioactive isotopes have half-lives that are less than 2.5 hours, and the majority of these have half-lives that are less than 5 minutes. Cadmium has 8 known meta states, with the most stable being ^{113m}Cd ($t_{½}$ = 14.1 years), ^{115m}Cd ($t_{½}$ = 44.6 days), and ^{117m}Cd ($t_{½}$ = 3.36 hours) [27].

The known isotopes of cadmium range in atomic mass from 94.950 u (^{95}Cd) to 131.946 u (^{132}Cd). For isotopes lighter than 112 u, the primary decay mode is electron capture and the dominant decay product is element 47 (silver). Heavier isotopes decay mostly through beta emission producing element 49 (indium) [28].

One isotope of cadmium, ^{113}Cd, absorbs neutrons with very high probability if they have an energy below the *cadmium cut-off* and transmits them otherwise. The cadmium cut-off is about 0.5 eV. Neutrons with energy below the cutoff are deemed slow neutrons, distinguishing them from intermediate and fast neutrons [29].

Cadmium is created via the long s-process in low-medium mass stars with masses of 0.6 to 10 solar masses, which lasts thousands of years. It requires a silver atom to capture a neutron and then undergo beta decay [30].

Toxicity of Cadmium

Cadmium particles in air can travel long distances before falling to the ground or water. It enters water and soil from waste disposal and spills or leaks at hazardous waste sites. Some cadmium dissolves in water. It doesn’t break down in the environment, but can change forms. Fish, plants, and animals take up cadmium from the environment. Cadmium stays in the body a very long time and can build up from many years of exposure to low levels. Environmental Protection Agency (EPA) limits drinking water: 5 ppb. EPA also limits how much cadmium can enter lakes, rivers, waste sites, and cropland and forbids cadmium in pesticides. Food and Drug Administration (FDA) limit in food colours: 15 ppm. Occupational Safety and Health Administration (OSHA) workplace air limit: 100µg/m^3 as cadmium fumes and 200µg/m^3 as cadmium dust. OSHA is planning to limit all cadmium compounds to either 1 or 5µg/m^3.

Acute effects of cadmium occur by breathing high levels dust or fumes and may cause throat dryness, cough, headache, vomiting, chest pain, extreme restlessness and irritability, pneumonitis, possibly bronchopneumonia and can cause death due to severe lung damage. Eating food or drinking water with very high levels (metal and compounds) increases salivation, severely irritates the stomach, leading to vomiting and diarrhea. Long term exposure to lower levels of cadmium in air, food, or water leads to a build up of cadmium in the kidneys and possible kidney disease. Other potential long term effects are lung damage and fragile bones, abdominal pain, choking and tenesmus. Cadmium salts are more toxic than those of zinc. The Department of Health and Human Services (DHHS) has determined that cadmium and cadmium compounds may reasonably be anticipated to be carcinogens.

1. 2. 3. Chromium

Chromium has three main forms viz, Cr(0), Cr(III), and Cr(VI). Cr(III) compounds are stable and occur naturally, in the environment. Cr(0) does not occur naturally and Cr(VI) occurs only rarely. Chromium compounds have no taste or odor. Cr(III) is an essential nutrient in our diet, but we need only a very small amount. Other forms of chromium are not needed by our bodies.

Waste streams containing heavy metals such as Cu, Zn, Ni, Pb, Cd, Cr are often encountered in various chemical industries. Among these heavy metals, pollution by chromium is of considerable concern as the metal is used in electroplating, leather tanning, metal finishing, and chromate preparation. Chromium occurs in aqueous systems in trivalent and hexavalent forms. But the latter form is of particular concern due to its greater toxicity. When chromium enters the gastric system, epigastric pain, nausea, vomiting, severe diarrhea, corrosion of skin, respiratory tract and lungs carcinoma are noticed. The discharge limit of chromium from industries is less than 1 mg/L. Chromium is hazardous to health when its limit in potable water exceeds 0.5 mg/L [31].

Chromium is a naturally occurring element found in rocks, soil, plants, animals, and in volcanic dust and gases. It is used in manufacturing chrome-steel or chrome-nickel-steel alloys (stainless steel) and other alloys, bricks in furnaces, and dyes and pigments, for greatly increasing resistance and durability of metals and chrome plating, leather tanning, and wood preserving. Manufacturing, disposal of products or chemicals containing chromium, or fossil fuel burning release chromium to the air, soil, and water. Particles settle from air in less than 10 days. It sticks strongly to soil particles; in water it sticks to dirt particles that fall to the bottom; only a small amount dissolves. Small amounts move from soil to groundwater.

Importance of Chromium

Due to an increase in population coupled with mining, extraction and use of various metals as different industrial and household materials, the extent of toxic metal ions in the environment is increasing gradually. The waste from metallurgical/mining sectors, in general, creates destabilization in the ecosystem, as most of the heavy metal ions are toxic to the living organisms. But some of these heavy metals, in traces, play significant role in the human metabolism. The demand of chromium has been increasing globally due to its extensive use in various metallurgical, chemical and leather tanning industries due to its various physico-chemical properties. Some of its important applications are enumerated below:

- Corrosion resistance property of chromium expanded its application in hardened steel, stainless steel and alloys.
- Electro-plating to produce a hard, shining surface and prevent corrosion.

- To impart a greenish tint to glass.
- Catalysts preparation.
- To prepare $K_2Cr_2O_7$ as an oxidizing agent.
- Yellow pigments (e.g. lead chromate).
- In the textile industries as a mordant.
- In the aircraft and other industries for anodizing and corrosion resistance.
- In refractory for aluminum forming bricks (as chromate) to give a defined shape as it has a high melting point, moderate thermal expansion and stable crystalline structure.
- In open-hearth steel melting furnaces as a major component due to its high melting point (1700-1900 ºC) and neutrality, being ideal for separating acidic and basic refractory in wall linings.
- In leather tanning.
- In industrial chemical synthesis.

Apart from industrial uses, Cr(III) plays an important role in our body. Without Cr(III) in our diet, the body loses its ability to use sugar, protein and fat properly, which may result in weight loss or impaired growth, improper function of nervous system and imbibe diabetic conditions. The best-known nutritional effect of chromium is to assist insulin in regulating blood sugar (glucose) levels in human body as established through radio tracing. Insulin is a protein hormone that is released into the blood when blood glucose level gets high. Insulin then binds to the receptor cells outside, causing them to absorb more glucose from blood, returning blood glucose levels to normal.

In the beginning of life the mineral chromium is important from the very earliest stage of life. Conception of new life begins a process of rapid cell duplication by division (mitosis) over and over again. This requires lots of energy. A substance named adenosine triphosphate (ATP) provides energy in human cells. ATP is the basic energy unit of the cell. If there is no ATP then there is no cell duplication. It is just that simple. That makes ATP a very simple priority for the healthy formation of life. Combining glucose (blood sugar) and oxygen produces ATP. Therefore, it is of utmost importance that glucose is efficiently provided for life to flourish. Chromium is essential for the insulin molecule to bring glucose into the cells for glycoloysis--the first step in ATP production.

Combining glucose (blood sugar) and oxygen produces ATP. Therefore, it is of utmost importance that glucose is efficiently provided for life to flourish. The pancreas produces insulin. Insulin delivers glucose to the cells in the body. Insulin is a carrier molecule. It is like a truck that transports glucose to cells throughout the body. An insulin receptor site is comparable to a loading dock. Chromium is like the dock-worker. This is where the glucose is unloaded and passed into the cell for production of ATP (energy).

Toxicity of Chromium (III) and Chromium (VI)

Cr(VI) is more toxic than Cr(III). On acidifying, chromates form $HCrO_4^-$ and orange red dichromate $Cr_2O_7^{2-}$. At pH 2-6,

$$HCrO_4^- \rightleftarrows Cr_2O_7^{2-}$$

Cr(III) compounds are ionic and contain Cr^{3+} and most stable compounds of chromium. Although this oxidation state is very stable in acidic solution, it is easily oxidized to Cr(VI) in alkaline solution.

Very small amounts of Cr(III) are in everyday foods. All forms of chromium can be toxic at high levels, but Cr(VI) is more toxic than Cr(III). Acute toxic effects occur when breathing very high levels of Cr(VI) in air that can damage and irritate your nose, lungs, stomach, and intestines. People who are allergic to chromium may also have asthma attacks after breathing high levels of either Cr(VI) or Cr(III). Long term exposures to high or moderate levels of Cr(VI) cause damage to the nose (bleeding, itching, sores) and lungs, and can increase your risk of non-cancer lung diseases. Ingesting very large amounts of chromium can cause stomach upsets and ulcers, convulsions, kidney and liver damage, and even death. Skin contact with liquids or solids containing Cr(VI) may lead to skin ulcers. Some people have allergic reactions including severe redness and swelling. Certain Cr(VI) compounds are known carcinogens. This is based on increased lung cancer in some workers who were exposed to chromium. Animal studies also indicate Cr(VI) is a carcinogen.

Harmful Effects of Cr (VI)

For quite some time, the chromite matrix was considered to be the most stable and hexavalent chromium pollution due to chromite mining or handling was thought to be impossible. Later, studies revealed that the Cr(III) lodged in chromite gets oxidized by arious physico-chemical and biological processes to produce Cr(VI).

The waste and effluent stream of chromite mines and processing units contain chromium in two oxidation states, i.e., Cr(VI) and Cr(III) in aqueous solution. Out of these, Cr(VI) is highly toxic in nature [32]. The first report on harmful effects of Cr(VI) appeared in 1930s because of the incidence of lung-cancer cases among workers in chromate handling industries. The relationship between trivalent and a hexavalent form of chromium is given by:

$$Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O + 1.33V$$

The difference in oxidizing potential of these two oxidation states show strong oxidizing power of the Cr(VI) species. On the other hand, high energy required to oxidize the trivalent form is not available with the biological systems and so almost all the Cr(VI) found in nature are derived from human activities. Cr(III), which generally occurs in the form of Cr(III), $Cr(OH)^{2+}$ or $Cr(OH)_2^{+}$, are adsorbed on the negatively charged soil particles and thus are less mobile. On the contrary, Cr(VI) is present in the aqueous solution in the form of dichromate ($Cr_2O_7^{-}$), hydro chromate ($HCrO_4^{-}$) or chromate (CrO_4^{2-}). These anionic species are generally poorly adsorbed by the negatively charged soil particles due to their repulsive electrostatic interaction. So, Cr(VI) is mobile and present in aqueous solution only. In experiments using cell culture, investigators found that Cr(VI) penetrates the cell membrane and gets into the cells much more easily than Cr(III). The later doesn't normally enter into cells because of its slightly bigger size as compared to Cr(VI) ions. The Cr(VI) inside the cell is reduced rapidly to Cr(III). The process of Cr(VI) reduction can create reactive oxygen (O^{-}) and other free radicals inside the cell. This combination of reactive intermediates has been postulated to be able to attack DNA leading to its damage. Since they are unstable, these intermediates are reduced to stable Cr(III), found on the DNA at the end of the process. DNA damage can lead to mutations, which in certain cancer-associated genes of the cell are believed to be the basis for initiating cancer.

Breathing in high levels of Cr(VI) (>2 µg/m3) containing dust particles in the form of compounds like chromic acid or chromium tri-oxide, can cause irritation to the respiratory system. The symptoms include running nose, sneezing, itching, nose bleeding, ulcers and damage to the nasal septum. These ailments are found in mining and industrial workers who handle Cr(VI) for a long period. A prolonged exposure of Cr(VI) is likely to cause allergic reaction consisting of severe redness and swelling of the skin leading to skin ulcer. In the animals that breathe high levels of Cr(VI), harmful effects on the respiratory system and a lower ability to fight diseases are noticed

1. 3. Industrial Effluent

Advances in science and technology have brought tremendous progress in many spheres of development, but the processes also have contributed to degradation of environment all over the globe due to very little attention paid to the treatment of industrial effluents. Industrial pollution continues to be a potential threat affecting the water. The discharge of non-biodegradable heavy metals into water stream is hazardous because the consumption of polluted water causes various health problems.

Water is the most vital element among the natural resources, and is crucial for the survival of all living organisms. The environment, economic growth and development of Bangladesh are all highly influenced by water - its regional and seasonal availability, and the quality of surface and groundwater. In terms of quality, the surface water of the country is unprotected from untreated industrial effluents and municipal wastewater, runoff pollution from chemical fertilizers and pesticides, and oil and lube spillage in the coastal area from the operation of sea and river ports. Water quality also depends on effluent types and discharge quantity from different type of industries, types of agrochemicals used in agriculture, and seasonal water flow and dilution capability by the river system.

Table 1: Literature Review- Industrial Effluent related articles

Location of sampling	**Metal ion Concentration, (mg/L)**			**pH**	**Reference**
	Pb(II)	**Cd(II)**	**Cr(III)**		
DEPZ, Bangladesh	0.021	<0.0045	<0.004	5.98	[33]
DEPZ, Bangladesh	0.21	0.06	0.43	-	[34]
Jakara wastewater channel, Nigeria	1.23 to 2.87	1.00 to 3.58	1.56 to 4.33	9.94	[35]
DEPZ, Bangladesh	<0.010	<0.003	0.27	7.84	[36]
Madina Tanary area, Chittagong	-	-	70.33 (Cr^{+6})	10.43	[37]
--	1.2- 3.2	-	-	8.6-10.5	[38]
Lexco Ltd. In Hazaribagh, Dhaka	6.5-0.37	-	5736-385 (Total Cr)	4.5-2.67	[39]
Musi river near Hyderabad, India	0.21	0.025	Trace amount	-	[40]
Safe limit for water	0.5	0.01	0.1	-	[41]

Table 2: National Standards- Waste Discharge Quality Standards for Industrial Units and Projects: Quality and Discharge point [42]

Parameter	**Unit**	**Location of final Disposal**		
		land surface water^1	**Public sewer**^{1}	**Irrigated land**^{1}
Temperature- Summer	^{0}C	40	40	40
Temperature- Winter	^{0}C	45	45	45
pH	-	6-9	6-9	6-9
Lead (Pb)	mg/L	0.1	0.1	0.1
Cadmium (Cd)	mg/L	0.05	0.5	0.5
Chromium (Hexavalent Cr^{+6})	mg/L	0.1	1.0	1.0
Chromium (Total Cr)	mg/L	0.5	1.0	1.0

Note: *Land surface water* refer to any pond, tank, water body, water hole, canal, river, spring or estuary, *Public Sewer* refers to any sewer connected with fully combined processing plant including primary and secondary treatment, *Irrigated Land* refers to an appropriately irrigated plantation area of specified crops based on quantity and quality of wastewater

1. 4. Different new technologies in heavy metals removal from Wastewater

The presence of large quantities of toxic metals such as mercury, lead, cadmium, zinc or others, poses serious health risks to humans, and this threat puts the scientific community under pressure to develop new methods to detect and eliminate toxic contaminants from wastewaters in efficient and economically viable ways.

This section provides details on the latest developments and efforts in general heavy metals removal from wastewater. We have discussed the following:

- Current Wastewater Treatment Process - Heavy Metals Removal
- New Technologies in Heavy Metals Removal from Wastewater,
- Metal Removal from Wastewater Using Peat
- A Novel Method for Heavy Metal Removal Using Fish Scales
- Seashells for Heavy Metals Clean-Up
- Toxic Heavy Metal Ions Removal from Waste Water by Membrane Filtration Of PGA-Based Nanoparticles
- Novel Biofiltration Methods for the Treatment of Heavy Metals from Industrial Wastewater
- Removal of Heavy Metals from Industrial Wastewaters by Adsorption onto Activated Carbon Prepared from an Agricultural Solid Waste
- Physico–Chemical Treatment Techniques for Wastewater Laden with Heavy Metals
- Microbial and Plant Derived Biomass for Removal of Heavy Metals from Wastewater
- Removal of Heavy Metals from Wastewater by Membrane Processes: A Comparative Study

- Low-Cost Adsorbents for Heavy Metals Uptake from Contaminated Water: A Review
- Current Wastewater Treatment Process - Heavy Metals Removal

The traditional method followed in industries to remove toxic heavy metal wastes is as follows:
A heavy metal (in the form of ion) can be removed from waste water, by adding to the waste water a metal scavenger together with at least one of sodium monosulfide, sodium polysulfides and sodium hydrogensulfide to form a metal ion containing floc. The resulting floc is then removed from the waste water by filtration. The metal scavenger contains at least one carbodithio group and/or at least one carbodithioate salt group as N-substituents per molecule.

- **New Technologies in Heavy Metals Removal from Wastewater**

i. Metal Removal from Wastewater Using Peat:

Peat has been investigated by several researchers as a sorbent for the capture of dissolved metals from waste streams [43]. The mechanism of metal ion binding to peat remains a controversial area with ion-exchange, complexation, and surface adsorption being the prevalent theories. Factors affecting adsorption include pH, loading rates, and the presence of competing metals. The optimum pH range for metals capture is generally 3.5–6.5. Although the presence of more than one metal in a solution creates competition for sorption sites and less of a particular ion may be bound, the total sorption capacity has been found to increase. Studies have also shown that metals removal is most efficient when the loading rates are low. In addition, recovery of metals and regeneration of the peat is possible using acid elution with little effect on peat’s sorption capacity.

ii. A Novel Method for Heavy Metal Removal Using Fish Scales:

Effective removal of metal ions from industrial wastewater by using fish scales was studied by Mustafiz et al [44]. A series of static tests was performed with 10 g of dried fish scale adsorbent pulverized to micron sizes of 37 or less. Such tests were conducted for lead ions (from lead nitrate solution) at concentrations of 25 ppm, 12.5 ppm, and 6.25 ppm. The dynamic equilibrium results were based on tests on 50 ppm of cobalt chloride solution (flow rate 1 ml/min), followed by 100 ppm of cobalt solution (flow rate 7 ml/min), and then a mixture of cobalt chloride ($CoCl_2$), lead nitrate ($Pb(NO_3)_2$), zinc nitrate hexahydrate ($Zn(NO_3)_2.6H2O$) and strontium nitrate ($Sr(NO_3)_2$) solutions. The proposed sorption technique offers an acceptable solution for removal of heavy metal ions from wastewater streams. The potential application of this study is an enormous energy cost savings in the electroplating industry, which requires the replacement of wastewater and the burial of metal sludge in landfills. Also, the trimming of energy costs in oil drilling and pipeline corrosion is possible by potential formation of biopolymers developed from "adsorbed scale".

iii. Removal of Heavy Metals by Seashells:

Köhler and his co-workers have found that pouring metal and acid-laden water over a bed of crushed clam or mussel shells provides an easy fix. The shells are made of aragonite, a form of calcium carbonate that readily swaps its calcium atoms in favor of heavy metals, locking them into a solid form. The shells are alkaline – a pH of 8.3 when dissolved – and needs to be maintained so by adding more shells [45].

iv. Toxic Heavy Metal Ions Removal from Waste Water by Membrane Filtration of PGA-based Nanoparticles:

Polymer enhanced ultrafiltration is a feasible method to remove metal ions from diluted waste water stream. Polyacids are widely investigated for this application. For separation of toxic heavy metal ions, including lead ions synthetic polymers and natural poly gamma glutamic acid (PGA) and other natural polymers have been investigated. In this study formation of nanoparticles of poly-gamma glutamic acid with bivalent metal ions is described. In aqueous solution the size of particles varies in the range of 50 nm to 350 nm depending on the pH. The stable nanoparticles were visualized by TEM measurements. The polyacid has high affinity and binds proportional toxic heavy metal ion. The polymer-lead complex was separated by ultrafiltration and the lead ions were concentrated in the retentate. The biopolymer is useful for treating waste water [46].

v. Novel Biofiltration Methods for the Treatment of Heavy Metals from Industrial Wastewater:

Most heavy metals are well-known toxic and carcinogenic agents and when discharged into the wastewater represent a serious threat to the human population and the fauna and flora of the receiving water bodies. In the present review paper, the sources have discussed the industrial source of heavy metals contamination in water, their toxic effects on the fauna and flora and the regulatory threshold limits of these heavy metals. The various parameters of the biofiltration processes, their mechanism for heavy metals removal along with the kinetics of biofilters and its modeling aspects have been discussed. The comparison of various physico-chemical treatment and the advantages of biofiltration over other conventional processes for treatment of heavy metals contaminated wastewater have also been discussed. The applications of genetic engineering in the modification of the microorganisms for increasing the efficiency of the biofiltration process for heavy metals removal have been critically analyzed. The results show that the efficiency of the process can be increased three to six folds with the application of recombinant microbial treatment [47].

vi. Removal of Heavy Metals from Industrial Wastewaters by Adsorption onto Activated Carbon Prepared From an Agricultural Solid Waste:

Activated carbon was prepared from coirpith by a chemical activation method and characterized by Kadirvelu et al [48] and the adsorption of toxic heavy metals, Hg(II), Pb(II), Cd(II), Ni(II), and Cu(II) was studied using synthetic solutions. It was found that the adsorption of toxic heavy metals from industrial wastewaters onto coirpith carbon was studied. The percent adsorption increased with increase in pH from 2 to 6 and remained constant up to 10. As coirpith is discarded as waste from coir processing industries, the resulting carbon is expected to be an economical product for the removal of toxic heavy metals from industrial wastewaters.

vii. Physico–Chemical Treatment Techniques for Wastewater Contaminated with Heavy Metals:

A number of physic-chemical methods have appeared in the literature for the treatment wastewater contaminated with heavy metals [49]. A particular focus is given to chemical precipitation, coagulation–flocculation, flotation, ion exchange and membrane filtration. Their operating conditions such as pH, dose required, initial metal concentration and treatment performance are presented. Ion exchange and membrane filtration methods are the most frequently studied and widely applied for the treatment of metal-contaminated wastewater. Ion exchange has achieved a complete removal of Cd(II), Cr(III), Cu(II), Ni(II) and Zn(II) with an initial concentration of 100 mg/L, respectively. The results are comparable to that of reverse osmosis (99% of Cd(II) rejection with an initial concentration of 200 mg/L). Lime precipitation has been found as one of the most effective means to treat inorganic effluent with a metal concentration of higher than 1000 mg/L. It is important to note that the overall treatment cost of metal-contaminated water varies, depending on the process employed and the local conditions. In general, the technical applicability, plant simplicity and cost-effectiveness are the key factors in selecting the most suitable treatment for inorganic effluent.

viii. Microbial and Plant Derived Biomass for Removal of Heavy Metals from Wastewater:

Discharge of heavy metals from metal processing industries is known to have adverse effects on the environment. Conventional treatment technologies for removal of heavy metals from aqueous solution are not economical and generate huge quantity of toxic chemical sludge. Biosorption of heavy metals by metabolically inactive non-living biomass of microbial or plant origin is an innovative and alternative technology for removal of these pollutants from aqueous solution. Due to unique chemical composition biomass sequesters metal ions by forming metal complexes from solution and obviates the necessity to maintain special growth-supporting conditions. Biomass of Aspergillus niger, Penicillium chrysogenum, Rhizopus nigricans, Ascophyllum nodosum, Sargassum natans, Chlorella fusca, Oscillatoria anguistissima, Bacillus firmus and Streptomyces sp. have highest metal adsorption capacities ranging from 5 to 641 mg g^{-1} mainly for Pb, Zn, Cd, Cr, Cu and Ni. Biomass generated as a by-product of fermentative processes offers great potential for adopting an economical metal-recovery system. The purpose of this paper is to review the available information on various attributes of utilization of microbial and plant derived biomass and explores the possibility of exploiting them for heavy metal remediation [50].

ix. Removal of Heavy Metals from Wastewater by Membrane Processes: A Comparative Study:

Wastewater containing copper and cadmium can be produced by several industries. The application of both reverse osmosis (RO) and nanofiltration (NF) technologies for the treatment of wastewater containing copper and cadmium ions to reduce fresh water consumption and environmental degradation was investigated. Synthetic wastewater samples containing Cu(II) and Cd(II) ions at various concentrations were prepared and subjected to treatment by RO and NF in the laboratory. The results showed that high removal efficiency of the heavy metals could be achieved by RO process (98% and 99% for copper and cadmium, respectively). NF, however, was capable of removing more than 90% of the copper ions existing in the feed water. The effectiveness of RO and NF membranes in treating wastewater containing more than one heavy metal was also investigated. The results showed that the RO membrane was capable of treating wastewater with an initial concentration of 500 ppm and reducing the ion concentration to about 3 ppm (99.4% removal), while the average removal efficiency of NF was 97%. The low level of the heavy metals concentration in permeate implies that water with good quality could be reclaimed for further reuse [51].

x. Low-Cost Adsorbents for Heavy Metals Uptake from Contaminated Water:

The technical feasibility of various low-cost adsorbents for heavy metal removal from contaminated water has been reviewed by Sandhya et al [52]. Instead of using commercial activated carbon, researchers have worked on inexpensive materials, such as chitosan, zeolites, and other adsorbents, which have high adsorption capacity and are locally available. The results of their removal performance are compared to that of activated carbon and are presented in this study. It is evident from our literature survey of about 100 papers that low-cost adsorbents have demonstrated outstanding removal capabilities for certain metal ions as compared to activated carbon. Adsorbents that stand out for high adsorption capacities are chitosan (815, 273, 250 mg/g of Hg2+, Cr6+, and Cd2+, respectively), zeolites (175 and 137 mg/g of Pb^{2+} and Cd^{2+}, respectively), waste slurry (1030, 560, 540 mg/g of Pb^{2+}, Hg^{2+}, and Cr^{6+}, respectively), and lignin (1865 mg/g of Pb^{2+}). These adsorbents are suitable for inorganic effluent treatment containing the metal ions mentioned previously. It is important to note that the adsorption capacities of the adsorbents presented in this paper vary, depending on the characteristics of the individual adsorbent, the extent of chemical modifications, and the concentration of adsorbate.

1.5 Adsorption Isotherm

1. 5. 1 Adsorption

Adsorption is the adhesion of atoms, ions, biomolecules or molecules of gas, liquid, or dissolved solids to a surface. This process creates a film of the adsorbate (the molecules or atoms being accumulated) on the surface of the adsorbent. It differs from absorption, in which a fluid permeates or is dissolved by a liquid or solid. The term sorption encompasses both processes, while desorption is the reverse of adsorption. It is a surface phenomenon.

Similar to surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements (be they ionic, covalent, or metallic) of the constituent atoms of the material are filled by other atoms in the material. However, atoms on the surface of the adsorbent are not wholly surrounded by other adsorbent atoms and therefore can attract adsorbates. The exact nature of the bonding depends on the details of the species involved, but the adsorption process is generally classified as physisorption (characteristic of weak van der Waals forces) or chemisorption (characteristic of covalent bonding). It may also occur due to electrostatic attraction [53].

Adsorption is present in many natural, physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, capturing and using waste heat to provide cold water for air conditioning and other process requirements (adsorption chillers), synthetic resins, increase storage capacity of carbide-derived carbons for tunable nanoporous carbon, and water purification. Adsorption, ion exchange, and chromatography are sorption processes in which certain adsorbates are selectively transferred from the fluid phase to the surface of insoluble, rigid particles suspended in a vessel or packed in a column.

1. 5. 2 Isotherms

Adsorption is usually described through isotherms, that is, the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid) at constant temperature. The quantity adsorbed is nearly always normalized by the mass of the adsorbent to allow comparison of different materials. There are basically two well established types of adsorption isotherm: the Langmuir adsorption isotherm and the Freundlich adsorption isotherm.

1. 5. 3 Langmuir Isotherm

The Langmuir equation (also known as the Langmuir isotherm, Langmuir adsorption equation or Hill-Langmuir equation) relates the coverage or adsorption of molecules on a solid surface to gas pressure or concentration of a medium above the solid surface at a fixed temperature. In 1916, Irving Langmuir published a new model isotherm for gases adsorbed to solids, which retained his name. It is a semi-empirical isotherm derived from a proposed kinetic mechanism. It is based on some assumptions:

1. The surface containing the adsorbing sites is perfectly flat plane with no corrugations (assume the surface is homogeneous).
2. The adsorbing gas adsorbs into an immobile state.
3. All sites are equivalent.
4. Each site can hold at most one molecule of A (mono-layer coverage only).
5. There are no interactions between adsorbate molecules on adjacent sites.

These five assumptions are seldom all true: there are always imperfections on the surface, adsorbed molecules are not necessarily inert, and the mechanism is clearly not the same for the very first molecules to adsorb to a surface as for the last. The fourth condition is the most troublesome, as frequently more molecules will adsorb to the monolayer; this problem is addressed by the BET isotherm for relatively flat (non-microporous) surfaces. The Langmuir isotherm is nonetheless the first choice for most models of adsorption, and has many applications in surface kinetics (usually called Langmuir-Hinshelwood kinetics) and thermodynamics.

Langmuir suggested that adsorption takes place through this mechanism:

$$A_g + S \rightleftharpoons A_{ad}$$

where A is a gas molecule and S is an adsorption site. The direct and inverse rate constants are k and k_{-1}. If we define surface coverage, θ, as the fraction of the adsorption sites occupied, in the equilibrium we have

$$K = \frac{k}{k_{-1}} = \frac{\theta}{(1-\theta)P}$$

Or $$\theta = \frac{KP}{1+KP}$$

where P is the partial pressure of the gas or the molar concentration of the solution. For very low pressures $\theta \approx KP$ and for high pressures $\theta \approx 1$.

θ is difficult to measure experimentally; usually, the adsorbate is a gas and the quantity adsorbed is given in moles, grams, or gas volumes at standard temperature and pressure (STP) per gram of adsorbent. If we call v_{mon} the STP volume of adsorbate required to form a monolayer on the adsorbent (per gram of adsorbent), $\theta = \frac{v}{v_{mon}}$ and we obtain an expression for a straight line:

$$\frac{1}{v} = \frac{1}{Kv_{mon}}\frac{1}{P} + \frac{1}{v_{mon}}$$

Through its slope and y-intercept we can obtain v_{mon} and K, which are constants for each adsorbent/adsorbate pair at a given temperature. v_{mon} is related to the number of adsorption sites through the ideal gas law. If we assume that the number of sites is just the whole area of the solid divided into the cross section of the adsorbate molecules, we can easily calculate the surface area of the adsorbent. The surface area of an adsorbent depends on its structure; the more pores it has, the greater the area, which has a big influence on reactions on surfaces.

The langmuir equation is simply expressed as

$$C_{ads} = \frac{K_L b C_e}{1 + b C_e}$$

It can be linearized as follows

$$\frac{1}{C_{ads}} = \frac{1}{K_L b C_e} + \frac{1}{K_L} ------(1)$$

Where

C_{ads} = amount of metal ions adsorbed (mg.g^{-1})

C_e = equilibrium concentration of metal ions (mg.L^{-1})

K_L= Langmuir Constant related to adsorption efficiency (kg.kg^{-1}) and

b = Langmuir Constant related to energy of adsorption (m^3/kg)

From the equation, $1/C_{ads}$ versus $1/Ce$ is a linear plot. We can determine the values of K_L and b from the slope, $1/K_L b$ and intercept, $1/K_L$ of the plot.

1. 5. 4 Freundlich Adsorption Isotherm

The Freundlich adsorption isotherm or Freundlich equation is an adsorption isotherm, which is a curve relating the concentration of a solute on the surface of an adsorbent, to the concentration of the solute in the liquid with which it is in contact. In 1909, Freundlich gave an empirical expression representing the isothermal variation of Adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure. This equation is known as Freundlich Adsorption Isotherm or Freundlich Adsorption equation.

The Freundlich empirical formula for gaseous adsorbates is expressed as

$$\frac{x}{m} = kP^{\frac{1}{n}}$$

where x is the quantity adsorbed, m is the mass of the adsorbent, P is the pressure of adsorbate and k and n are empirical constants for each adsorbent-adsorbate pair at a given temperature. The function has an asymptotic maximum as pressure increases without bound. As the temperature increases, the constants k and n change to reflect the empirical observation that the quantity adsorbed rises more slowly and higher pressures are required to saturate the surface.

The Freundlich Adsorption Isotherm for liquid is mathematically expressed as

$$C_{ads} = K_f C_e^{\frac{1}{n}}$$

It is also written as

$$\log C_{ads} = \log K_f + \tfrac{1}{n} \log C_e - - - - - - (2)$$

Where

C_{ads} = amount of metal ions adsorbed (mg. g^{-1})

C_e = equilibrium concentration of metal ions in solution (mg. L^{-1})

K_f = Freundlich Constant

$1/n$ = Freundlich Constant

K_f and $1/n$ are constants incorporating all factors affecting the adsorption capacity and intensity of adsorption, respectively at a particular temperature. log C_{ads} versus log Ce is a linear plot. Through its slop and intercept, we can obtain the values of n and K_f . Experimentally it was determined that extent of adsorption varies directly with pressure till saturation pressure Ps is reached. Beyond that point rate of adsorption saturates even after applying higher pressure. Thus Freundlich Adsorption Isotherm failed at higher pressure.

1. 6 Adsorption Kinetics

The study of adsorption dynamics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface. The kinetics of metal ions adsorption on the bioadsorbents are analysed using pseudo first-order pseudo second-order kinetic models [54, 55]. The conformity between experimental data and the model predicted values is expressed by the correlation coefficients (R^2, values close or equal to 1). A relatively high R^2 value indicates that the model successfully describes the kinetics of metal ions adsorption.

The Pseudo First-order Equation

The pseudo first-order equation (Lagergren, 1898) is generally expressed as follows:

$$\frac{dc_t}{dt} = k_1\left(C_e - C_t\right)$$

Where C_e and C_t are the adsorption capacity at equilibrium and at time t, respectively ($\mathrm{mg \cdot g^{-1}}$), k_1 is the rate constant of pseudo first-order adsorption ($\mathrm{l \cdot min^{-1}}$).

After integration and applying boundary conditions $t = 0$ to $t = t$ and $C_t = 0$ to $C_t = C_t$, the integrated form becomes:

$$\log\left(C_e - C_t\right) = \log\left(C_e\right) - \frac{k_1}{2.303} t - - - - - - - - \left(3\right)$$

The value of log $(Ce - Ct)$ is linearly correlated with t. The plot of log $(Ce - Ct)$ vs. t should give a linear relationship from which k_1 and Ce can be determined from the slope and intercept of the plot, respectively.

The Pseudo Second-order Equation

The pseudo second-order adsorption kinetic rate equation is expressed as [55]:

$$\frac{dc_t}{dt} = k_2\left(C_e - C_t\right)^2$$

Where k_2 is the rate constant of pseudo second-order adsorption (g·mg^{-1}·min^{-1}).

For the boundary conditions $t = 0$ to $t = t$ and $C_t = 0$ to $C_t = C_t$, the integrated form of the above Equation becomes:

$$\frac{1}{(C_e - C_t)} = \frac{1}{C_e} + kt$$

which is the integrated rate law for a pseudo second-order reaction. This equation can be rearranged to obtain the following Eq. which has a linear form:

$$\left(\frac{t}{C_t}\right) = \frac{1}{k_2 C_e^2} + \frac{1}{C_e}(t) - - - - (4)$$

If the initial adsorption rate, h (mg·g^{-1}·min^{-1}) is:

$$h = k_2 C_e^2$$

Then the Eq. (4) becomes:

$$\left(\frac{t}{C_t}\right) = \frac{1}{h} + \frac{1}{C_e}(t)$$

The plot of (t/C_t) *vs* t of Eq. (4) should give a linear relationship from which C_e and k_2 can be determined from the slope and intercept of the plot, respectively.

2 Literature Review

2.1 Harmful Effect of Heavy Metals:

Ever increasing industrial activity is the main culprit behind most environmental pollution problems and ecosystem damage, coming from the accumulation of pollutants such as toxic metals chromium, copper, lead, cadmium, zinc, nickel, etc. [56]. Contamination of soils, groundwater, sediments, surface water and air with hazardous and toxic chemicals poses significant problems for both human health and the environment [57]. Heavy metals are considered to be particularly dangerous pollutants. Their presence in the wastewater of several industrial processes, such as electroplating, metal finishing, metallurgical work, tanning, chemical manufacturing, mining and battery manufacturing, has brought about more environmental concerns due to their toxicity even at low concentrations [58–59]. In view of the human health impacts, each metal imparts different effects and symptoms. Chromium [60] can cause cancer in the digestive tract and lungs [61], while manganese (Mn) triggers neurotoxicity, low hemoglobin levels, and gastrointestinal accumulation [62]. As another example, copper consumption in high doses brings about serious toxicological concerns since it can be deposited in the brain, skin, liver, pancreas, and myocardium [63], and initiates intestinal distress, kidney damage and anemia [64]. Lead (Pb) has been cited as one of the three most toxic heavy metals that have latent long-term negative impacts on health, causing anemia, encephalopathy, hepatitis and nephritic syndrome [65]. Cadmium also exposes human health to severe risks, as it can provoke cancer, kidney damage, mucous membrane destruction, vomiting, diarrhea, bone damage, and itai-itai disease, as well as affect the production of progesterone and testosterone [66].

2.2 Removal of Heavy Metals from Water and Wastewater:

Several competitor technologies exist to eliminate heavy metals from industrial wastewater, including reduction followed by adsorption on miscellaneous adsorbents [67, 68], supercritical fluid extraction [69], ion exchange [70], ion flotation[71], electrocoagulation [72], high-gradient magnetic separation[73], micellar-enhanced ultrafiltrationtc [74] etc.. Most methods seem to be almost equally effective. However, further consideration of suitability places a large portion of them outside of industrial scale applications due to the high capital investment and operational costs involved. Specifically speaking, the most effective and versatile technique for heavy metal removal, even at very low concentrations, is adsorption. However, the high price of adsorbents (usually activated carbon) is regarded as the major obstacle for industrial application. From an economic point of view, it is infeasible to utilize activated carbon for commercial wastewater treatment. To that end, the focus of heavy metal adsorption studies has been altered toward natural materials that are available in vast amounts, as well as certain waste products from industrial and agricultural operations [75].

2.3 Biosorption of Heavy Metals:

Based upon the metal binding capacities of various biological materials, biosorption can separate heavy metals from wastewater [76]. Lately, biosorption has emerged as a cost-effective and efficient alternative for application to low strength wastewaters [77]. Biosorption, a term used here to describe the removal of heavy metals using a passive binding process with nonliving microorganisms including bacteria, fungi, and yeasts [78], and other biomass types that are capable of efficiently collecting heavy metals. Obviously, some of the advantages biosorption has over conventional treatment methods include low cost, high efficiency for dilute concentration solutions, a minimal amount of chemical and/or biological sludge, no additional nutrients required and the possibility of biosorbent regeneration and metal recovery [79]. The sorption of heavy metals onto these biomaterials is attributed to their constituents, which are mainly proteins, carbohydrates and phenolic compounds, since they contain functional groups such as carboxylates, hydroxyls and amines, which are able to attach to the metal ions [80].

Heavy metal accumulation in aquatic organisms, which is an active process involving metabolic activity within living organisms, has been studied by several researchers since 1978 [81-82]. Biosorption onto biomass, an entirely different process from bioaccumulation, was pioneered by Volesky's group from McGill University in 1981 [83]. At present, the biosorption field has been enriched by a vast amount of studies published in different journals. Although in the beginning most researchers focused their efforts upon heavy metal accumulation and concentration within living organisms [84, 85], upon noticing that dead biomass possesses high metal-sorbing potential [86], their interest shifted to biosorption [86 - 90]. This is mainly due to the abundant availability, adsorption capacity and economic value of agricultural, plant tissue and industrial wastes, which has made them the main subject for biosorption research during the last decade [91-93].

Several reviews are available that discuss the use of biosorbents for the treatment of water and wastewater containing heavy metals [94 -98].

2.4. Agricultural Waste and Other Cellulose Materials as Alternative Adsorbents:

Despite the availability of numerous techniques for the treatment of effluents with heavy metals, adsorption is constantly viewed as a highly effective technique for this purpose, especially in low metal concentration solutions.

Agricultural by-products are mostly composed of lignin and cellulose, as well as other polar functional group-containing compounds, which include alcohols, aldehydes, ketones, carboxylates phenols and ethers. These groups are able to bind heavy metals through replacement of hydrogen ions with metal ions in solution or by donation of an electron pair from these groups to form complexes with metal ions in solution [99].

The capability of several cheap agro-based materials, namely almond shell (AS), crushed coconut shell (CS), ground nut shell (GS), Tamarindus indica seed (TS), and walnut shell (WS), for Cr(VI) subtraction have been evaluated [100]. By comparing the adsorption capacity of five low cost sorbents, Agarwal et al. [32] concluded that the use of tamarind seed as an alternative adsorbent is more economical and worthwhile than other conventional methods. They also noted that the removal of Cr(VI) ions by tamarind seed is significantly decreased with an increase in pH, slightly decreased with ionic strength enhancement and enhanced with rising temperature. It is suggested that chemisorption is the most plausible mechanism involved.

Azadirachta indica (neem) is a typical tree in the mahogany family of Meliciae. Products derived from neem have proven to possess therapeutic value such as anthelmintic, antifungal, antidiabetic, antibacterial, antiviral, anti-infertility and sedative activities. Several researchers have investigated the prospects of neem leaf as an alternative adsorbent for Cr(VI), Cd(II) and Pb(II) [101–106]. Sharma and Bhattacharyya [102] utilized Azadirachta indica (Neem Leaf Powder) to extract chromium (VI) from solution. The adsorption was carried out in a batch process using different concentrations of metal ions in aqueous solution in parallel with variation in the adsorbent amount, pH, agitation time and temperature. The suitability criteria of the adsorbent were checked by the Langmuir and Freundlich isotherms, and also by various equilibrium kinetic data. On the basis of the Langmuir model, they obtained an adsorption capacity of neem leaf powder for Cr(VI) of 0.0028 mmol/g. A relatively low amount of Azadirachta indica (Neem Leaf Powder) (1.6 g dm^{-3}) could remove as much as 87% of Cr(VI) from a dilute solution (0.137 mmol/L) during a 300 min period at 300K. The optimum pH range in their study was 4.5–7.5. In a separate study, Babu and Gupta [101] also exploited activated Azadirachta indica (Neem Leaf Powder) as a biosorbent. By modifying the physical structure and surface chemistry of the neem leaf via an activation process, the adsorption capacity could be significantly enhanced.

Azadirachta indica (Neem Leaf Powder) was considered as a good adsorbent for cadmium from simulated wastewater [106]. In the adsorption of Cd(II) on Azadirachta indica (Neem Leaf Powder), pH had a considerable effect upon the removal percentage. A rise of pH from 4 to 9.5 resulted in an 11-fold enhancement of removal efficiency (8.8–93.6%). While the removal performance was better at higher pH, the effectiveness of Azadirachta indica (Neem Leaf Powder) to remove Cd(II) is still questionable, since no further information about the Cd(II) removal percentage caused exclusively by adsorption or precipitation is given. At high pH (above 8.6), it is likely that Cd(II) precipitates into its hydroxide, since the initial concentration used in their study (0.325 mmol/L) already surpasses the thermodynamic solubility limit of Cd(II) (around 0.07mmol/L) [107]. Therefore, the 11-fold enhancement of removal efficiency of Cd(II) would be better attributed to the higher extent of Cd(II) precipitation as its hydroxide at higher pH rather than the adsorption process. Chaff is an agricultural by-product that contains fiber and protein along with some functional groups, and is mainly given to livestock and poultry as food [108]. Numerous functional groups such as carboxylates, hydroxyls, amidogens, etc. are also encountered within chaff. Han et al. [108] performed a sorption process with chaff in a fixed-bed column. Several operation variables, represented by pH, flow rate, influent concentration of solution and co-existing ions were varied to reveal its effect on the removal performance. In addition, adsorption and desorption recycles of chaff were tried to arrive at a conclusion that their reuse would be feasible.

3 Experimental

3.1 Chemical and Reagents

All chemicals and reagents used for this research work were of analytical grade. Distilled and deionized (Water Distillation & Deionized Set, e.g, Aquatron A8000) water was used for the preparation of standard solutions and dilution of the samples. The reference standards are Cadmium (Cd), Fluka Chemika 20895, Germany; Chromium [III] (Cr), Fluka Chemika 27067, Switzerland and Lead (Pb), Fluka Chemika 15314, Switzerland.

3.2 Apparatus

The lists of apparatus are as follows:

1. Analytical Balance (METLER AE 200, Switzerland.
2. Shaker (GFL 3017, Germany)
3. Micropipette (variable volume) 0.2ml, 1 ml (Eppendorf)
4. Pipette and tips (Eppendorf)
5. Filter paper (Whatman No.1)
6. AAS : AA-6300 (SHIMADZU)
7. Auto sampler : ASC6100 (SHIMADZU)
8. Software: WizAArd software (SHIMADZU)
9. Hollow Cathode Lamp of Cd, Cr, Pb (HAMAMATSU PHONICS K.K)
10. Gases: Acetylene + Air

Optics Parameters, Atomizer/Gas Flow Rate Setup:

Pb:

Comment: Flame

Wavelength: 283.3 nm

Slit Width: 0.7 nm

Lamp Mode: BGC-D2

Lamp Current Low: 10mA

Burner Height: 7mm

Burner Angle: 0 degree

Flame Type: Air- C_2H_2

Fuel Gas: 2.0L/min

Support Gas: 15.0 L/min

Cd:

Comment: Flame

Wavelength: 228.8 nm

Slit Width: 0.7 nm

Lamp Mode: BGC-D2

Lamp Current Low: 8 mA

Burner Height: 7 mm

Burner Angle: 0 degree

Flame Type: Air- C_2H_2

Fuel Gas: 1.8 L/min

Support Gas: 15.0 L/min

Cr:

Comment: Flame

Wavelength: 357.9 nm

Slit Width: 0.7 nm

Lamp Mode: BGC-D2

Lamp Current Low: 10 mA

Burner Height: 9 mm

Burner Angle: 0 degree

Flame Type: Air- C_2H_2

Fuel Gas: 2.8 L/min

Figure 1: Atomic Absorption Spectroscopy

3.3 Preparation of the Adsorbent

Neem Leaves (Azadirachata Indica) and Jute (Corchorus Capsularis) Sticks were collected from Sherpur District in Bangladesh then washed thrice with tap water to remove dust and water soluble impurities and are dried until the leaves and sticks become crisp. The dried leaves and sticks are powdered. Then the neem leaf powder (NLP) and jute sticks powder (JSP) are sieved to achieve uniform size. The resulting NLP and JSP fractions are preserved in glass bottles for use as an adsorbent. Nut Shell (Arachis hypogaea) was collected from Dhaka, Bangladesh and similarly was prepared nut shell powder (NSP). The bio-adsorbents were chosen keeping in view low cost, easily available, safety to health and ease of application.

Figure 2: Jute Stick Powder (JSP)

Figure 3: Neem Leaf Powder (NLP)


2011/12/07

Figure 4: Nut Shell Powder (NSP)

3.4 Preparation of Standard Solution

Stock Solution (1000 ppm): The standard solutions are Cadmium (Cd), Fluka Chemika 20895, Germany; Chromium [III] (Cr), Fluka Chemika 27067, Switzerland and Lead (Pb), Fluka Chemika 15314, Switzerland. The concentration of these solutions is 1000 ppm and these are stock solutions.

Intermediate Solution (100 ppm): Stock solutions are diluted and prepared intermediate solution using Deionized water.

Standard Solutions: Intermediate solutions are diluted and prepared standard solutions of 0.5 ppm, 1 ppm, 2 ppm , 4ppm, 6 ppm , 8ppm and 10 ppm.

3.5 Preparation of Calibration Curve

100 ml standard solutions of different concentration such as 0.5 ppm, 1 ppm, 2 ppm , 4 ppm, were use for calibration curve. For each concentration, four replicate measurements were performed and average values were used for calibration curve. The calibration curve was straight line and it follows the Beer- Lambert law.

3.6 Determination of Heavy Metals (Pb. Cd, Cr) from Wastewater Samples

The water samples were digested as follows. The samples (100cm^3) were transferred into a beaker and 5ml concentrated HNO_3 was added. The beaker with the content was placed on a hot plate and evaporated down to about 20ml. The beakers were cooled and another 5ml of concentrated HNO_3 was added. The beakers were covered with watch glass and returned to the hot plate. The heating was continued, and then small portion of HNO_3 was added until the solutions appear light coloured and clear. The beaker wall and watch glass were washed with distilled water and the samples were filtered to remove some insoluble materials that could clog the atomizer. The volume of the samples was adjusted to 100 cm3 with distilled water [109]. A blank sample was digested so as to allow a blank correction to be made. This was done by transferring 100ml of distilled water into a beaker and digested as described above.

Determination of Pb, Cd and Cr were made directly on each final solution using Atomic Absorption Spectroscopy (AAS), AA-6300, SHIMADZU, Japan.

3. 7 Batch Equilibration Method

The adsorption experiments were carried out in a batch process at 25°C temperature. The known weight of adsorbent material was added to 100 mL of metal ion solutions with an initial concentration from 4.0 mg/L- 10.0mg/L. The contents were shaken thoroughly using a mechanical shaker (model: GFL-3017, Germany).The solution was then filtered at preset time intervals and the residual metal ion concentration was measured by using Atomic Absorption Spectroscopy (AAS) with ASC-3100 of model AA-6300, SHIMADZU, JAPAN and WizAArd software (SHIMADZU).

3. 8. Column Equilibration Method

In the column study, a three layer column was prepared. The first layer was of normal sand, second of the desired adsorbent and the last (or down layer) was also of normal sand. Before passing the metal ion solution through the column, deionized water was passed in a down flow direction to wet the beds completely [110 -111]. In every step, 1.0 g of adsorbent was used in the column with height 10 cm and diameter 4 cm [112]. The same concentrated (6.0mg/L) solution was used for all adsorbents. Each solution was run several times for equilibrium.

3. 9 Dosage of Adsorbents

The various doses consisting of the adsorbents respectively mixed with metal ion solutions and the mixture was agitated in a mechanical shaker (model: GFL-3017, Germany). The adsorption capacities for different doses were determined at definite time intervals by keeping all other factors constant.

3. 10 Initial Concentration of Metal ion

Experiments were conducted with different initial concentrations of metal ions ranging from 4.0 mg/L- 10.0mg/L. All other factors have kept constant.

3.11 Contact Time

The effect of period of contact on the removal of the metal ion on adsorbent in a single cycle was determined by keeping particle size, initial concentration, dosage, pH and concentration of other ions constant.

3. 12. pH

Adsorption experiments were carried out at pH 2, 3, 4, 5, 6, 7, 8 and 9. The acidic and alkaline pH of the media was maintained by adding the required amounts of dilute hydrochloric acid and sodium hydroxide solutions. The parameters like particle size of the adsorbents, metal ion concentration, dosage of the adsorbents and concentration of other ions have kept constant while carrying out the experiments. The pH of the samples was determined using Hanna HI 2211 bench top pH meter. The pH meter was calibrated with 4.01 and 9.18 buffers.

3.13 Desorption studies

Desorption experiments were performed in order to estimate the releasing capacity of metal ion from NLP, NSP and JSP surfaces. This studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the metal ions. The adsorbent saturated with different adsorbed amount of metal ions were dried at 60^0 C and then 0.5 g of these samples were added in a conical flask containing 100 mL deionized water and then100 mL 0.1M HCl under constant temperature of 25 ^{0}C. The resulting suspension was mechanically agitated for 1 h with a stirring and centrifuged. Supernatant solutions were analyzed for their metal ions content with AAS.

```
Cd(228.8nm)
File Comment:


Comment:
    Flame

Instrument Information
    Device Name:                   AA

    Type       Model Name   ROM Version S/N
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    ASC        ASC-6000     1.75        A30324302205OP
    GFA

Optics Parameters
    Element:                       Cd
    Socket #:                      3
    Lamp Current Low(mA):          8
    Wavelength(nm):                228.8
    Slit Width(nm):                0.7
    Lamp Mode:                     BGC-D2

Atomizer/Gas Flow Rate Setup
    Fuel Gas Flow Rate(L/min):     1.8
    Support Gas Flow Rate (L/min): 15.0
    Flame Type:                    Air-C2H2
    Burner Height(mm):               7
    Burner Angle(degree):            0

Measurement Parameters
    Order:                         1st
    Zero Intercept:                Non-Pass
    Conc. Unit:                    ppm
    Repetition Sequence:           SM-SM-...
    Pre-Spray Time (sec):          3
    Integration Time (sec):        5
    Response Time:                 1

               Num Reps.  Max Reps.  RSD Limit  SD Limit
    Blank          3          4       99.90     0.0000
    Standard       3          4        2.00     0.0000
    Sample         3          4        2.00     0.0000
    Reslope        1          1       99.90     0.0000

QA/QC Parameters
    IDL                            0.0000
    CRDL                           0.0000

    TV Method                      Calibration Curve
    Order                          1st
    Zero Intercept:                Non-Pass
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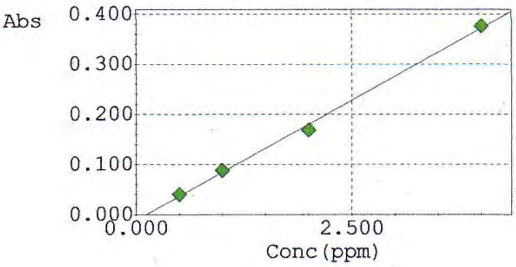
Calibration Curve (C# : 01)



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2.0000	0.1686
4.0000	0.3763

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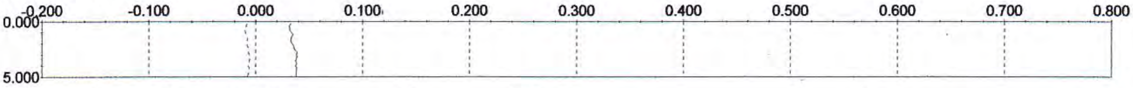
r=0.9986

std-1 : STD



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Time	User Name	Device Name
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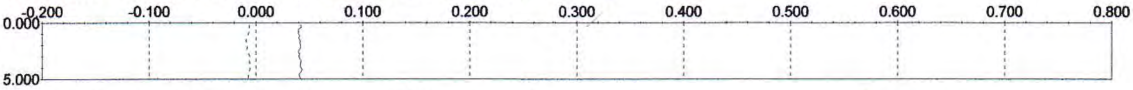

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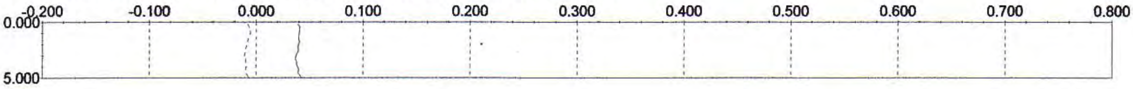

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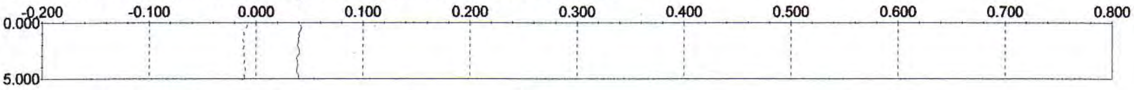

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Time	User Name	Device Name
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std-1 : STD Average

True Value	Conc.	Abs.	BG	Pos.
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%RSD	SD	%R	C#
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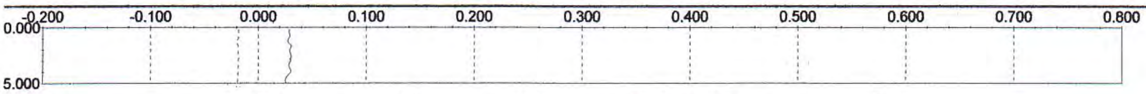

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_ M _ ___________ Conc.      Abs.     BG       ActualConc.  __ Date
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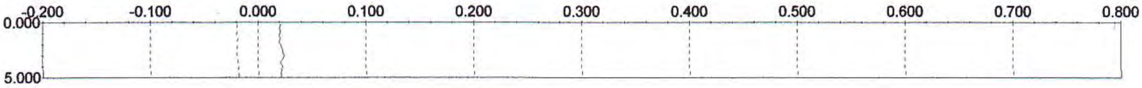
Time                  User Name              Device Name
12:21:00 PM(+0600)    System Administrator   AA
```

4 ppm1h : UNK Average

```
_ _________   Conc.      Abs.     BG      Pos. WF           VF       DF
                0.3996  0.0269  -0.0180  2       1.000000    1.00     1.00

CF          ActualConc.   Actual Conc. Unit  %RSD     SD              C#  SG#
  1.000000    0.3996       ppm                  1.55      0.0004   __  01  1
```

4 ppm 2h : UNK



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Time                  User Name              Device Name
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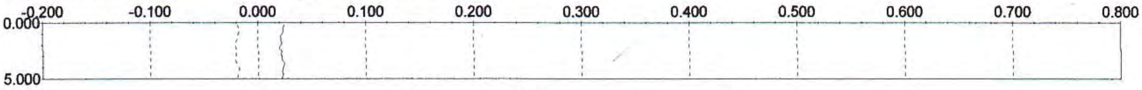

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Time                  User Name              Device Name
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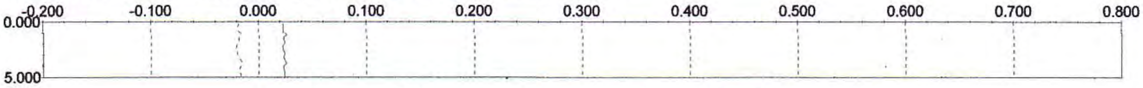

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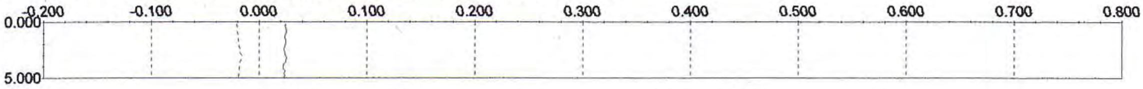

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Time                  User Name              Device Name
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4 ppm 2h : UNK Average

```
_ _________   Conc.      Abs.     BG      Pos. WF           VF       DF
                0.3495  0.0221  -0.0186  3       1.000000    1.00     1.00

CF          ActualConc.   Actual Conc. Unit  %RSD     SD              C#  SG#
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Cr(357.9nm)

File Comment:

Comment:
Flame

Instrument Information

Device Name: AA

Type	Model Name	ROM Version	S/N
AA	AA-6300	1.06	A30524300818
ASC	ASC-6000	1.75	A30324302205OP
GFA			

Optics Parameters

Element: Cr
Socket #: 3
Lamp Current Low(mA): 10
Wavelength(nm): 357.9
Slit Width(nm): 0.7
Lamp Mode: BGC-D2

Atomizer/Gas Flow Rate Setup

Fuel Gas Flow Rate(L/min): 2.8
Support Gas Flow Rate (L/min): 15.0
Flame Type: Air-C2H2
Burner Height(mm): 9
Burner Angle(degree): 0

Measurement Parameters

Order: 1st
Zero Intercept: Non-Pass
Conc. Unit: ppm
Repetition Sequence: SM-SM-...
Pre-Spray Time (sec): 3
Integration Time (sec): 5
Response Time: 1

	Num Reps.	Max Reps.	RSD Limit	SD Limit
Blank	3	4	99.90	0.0000
Standard	3	4	2.00	0.0000
Sample	3	4	2.00	0.0000
Reslope	1	1	99.90	0.0000

QA/QC Parameters

IDL 0.0000
CRDL 0.0000

TV Method Calibration Curve
Order 1st
Zero Intercept: Non-Pass

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Calibration Curve (C# : 01)
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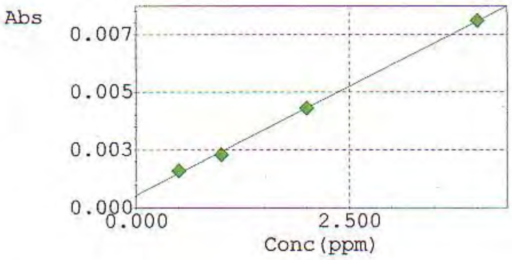

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2.0000	0.0043
4.0000	0.0081

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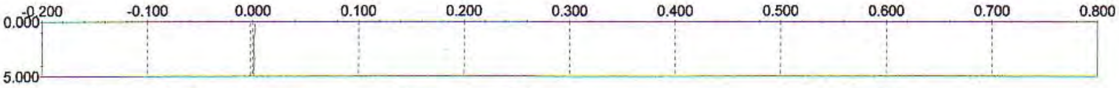
r=0.9994
```

STD-1 : STD



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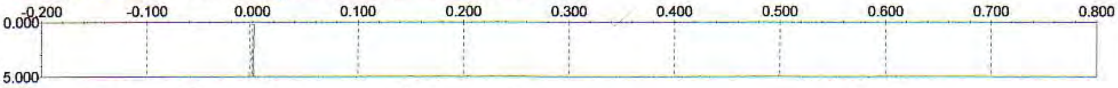

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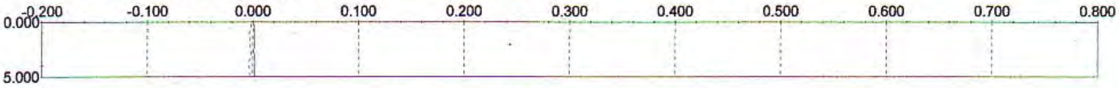

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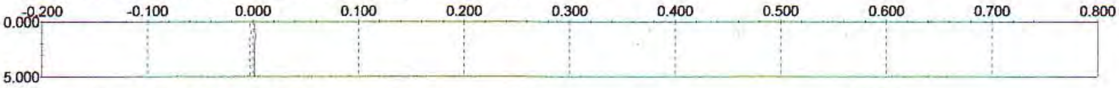

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Time                User Name             Device Name
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STD-1 : STD Average

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                    %RSD   SD         %R      C#
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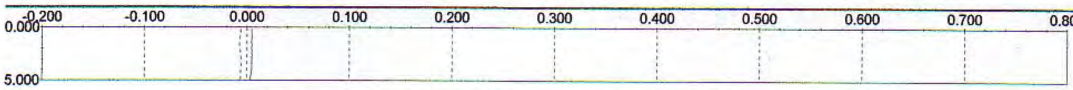

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Time                User Name             Device Name
3:11:51 PM(+0600)  System Administrator  AA
BLK-PH-2 : UNK Average
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CF          ActualConc.  Actual Conc. Unit %RSD      SD          C#  SG#
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___
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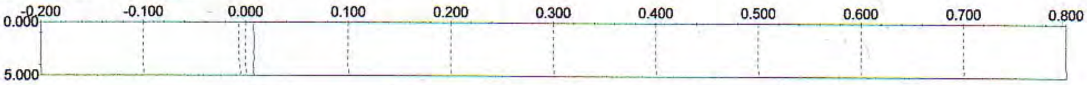
NUT-PH-7 : UNK



```
X
X _ _ __________ Conc.    Abs.    BG       ActualConc.  __ Date
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Time                User Name             Device Name
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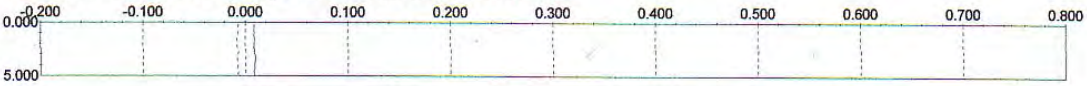
```



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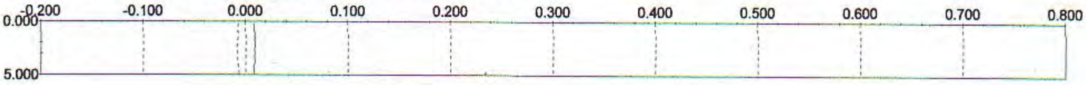

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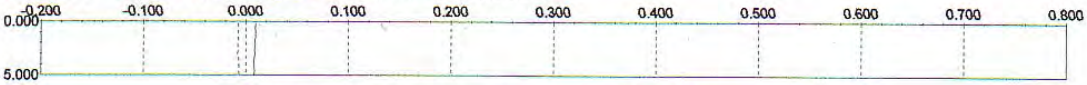

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CF          ActualConc.  Actual Conc. Unit %RSD      SD          C#  SG#
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___
```

```
Pb(283.3nm)
File Comment:


Comment:
    Flame

Instrument Information
    Device Name:                   AA

    Type       Model Name   ROM Version S/N
    AA         AA-6300      1.06        A30524300818
    ASC        ASC-6000     1.75        A30324302205OP
    GFA

Optics Parameters
    Element:                       Pb
    Socket #:                      6
    Lamp Current Low(mA):          10
    Wavelength(nm):                283.3
    Slit Width(nm):                0.7
    Lamp Mode:                     BGC-D2

Atomizer/Gas Flow Rate Setup
    Fuel Gas Flow Rate(L/min):     2.0
    Support Gas Flow Rate (L/min): 15.0
    Flame Type:                    Air-C2H2
    Burner Height(mm):               7
    Burner Angle(degree):            0

Measurement Parameters
    Order:                         1st
    Zero Intercept:                Non-Pass
    Conc. Unit:                    ppm
    Repetition Sequence:           SM-SM-...
    Pre-Spray Time (sec):          3
    Integration Time (sec):        5
    Response Time:                 1

               Num Reps.  Max Reps.  RSD Limit  SD Limit
    Blank          1          1        99.90    0.0000
    Standard       1          1        99.90    0.0000
    Sample         1          1        99.90    0.0000
    Reslope        1          1        99.90    0.0000

QA/QC Parameters
    IDL                            0.0000
    CRDL                           0.0000

    TV Method                      Calibration Curve
    Order                          1st
    Zero Intercept:                Non-Pass
```

```
Calibration Curve (C# : 01)
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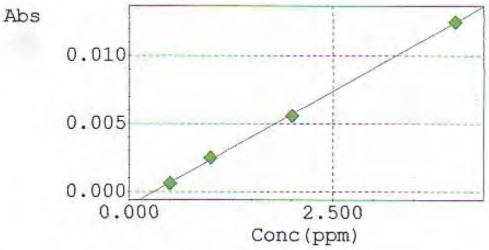

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Conc          Abs
(ppm)
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    2.0000        0.0056
    4.0000        0.0125

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r=0.9997
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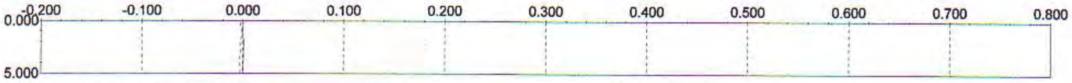
STD-1 : STD



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                      %R     C#            Date       Time                  User Name
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Device Name
AA
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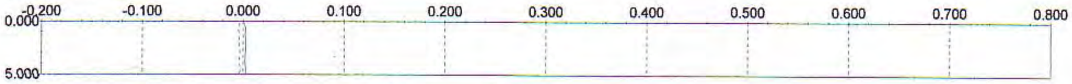
STD-2 : STD



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                      %R     C#            Date       Time                  User Name
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Device Name
AA
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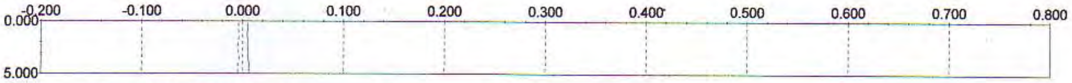
STD-3 : STD



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                      %R     C#            Date       Time                  User Name
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Device Name
AA
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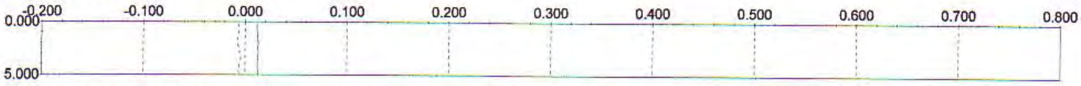
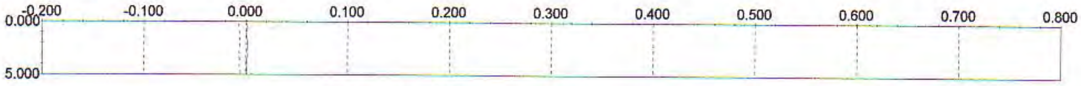
STD-4 : STD



```
_ _ _ True Value Conc.      Abs.    BG      Pos. _ _ _ _ _ _____________
      4.0000        4.0090  0.0125  -0.0059 R4
_________________ %R     C# _ _  Date      Time                User Name
                  100.2  01      8/24/2011 10:13:30 AM(+0600)  System Administrato:
Device Name
AA
```

BLK : BLK



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_________________ _ _ _ _ _  Date      Time               User Name
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Device Name
AA
```

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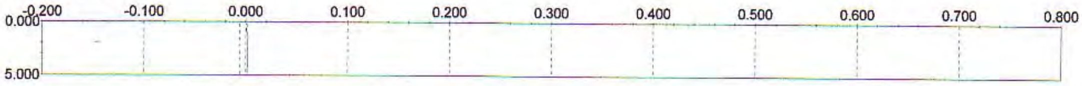

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Time                  User Name             Device Name
10:14:49 AM(+0600)    System Administrator  AA
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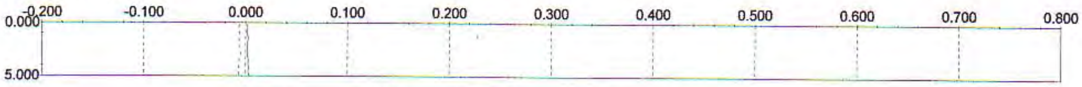

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_ _ _ ___________ Conc.   Abs.    BG      Pos. WF          VF     DF
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Time                  User Name             Device Name
10:15:28 AM(+0600)    System Administrator  AA
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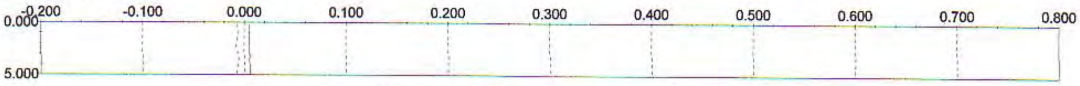
TS-3 : UNK



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Time                  User Name             Device Name
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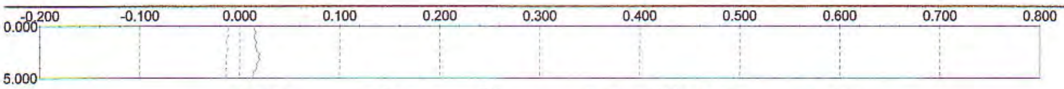

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Time                     User Name                 Device Name
11:42:30 AM(+0600)  System Administrator AA
6ppm-jt : UNK Average
                 Conc.     Abs.    BG       Pos. WF              VF       DF
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CF              ActualConc.  Actual Conc. Unit %RSD       SD               C#  SG#
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6ppm-nt : UNK
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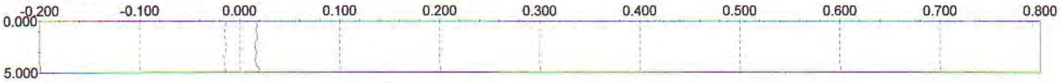

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Time                     User Name                 Device Name
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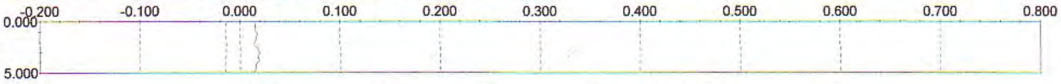

```
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Time                     User Name                 Device Name
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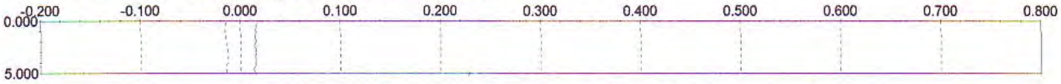

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Time                     User Name                 Device Name
11:43:27 AM(+0600)  System Administrator AA
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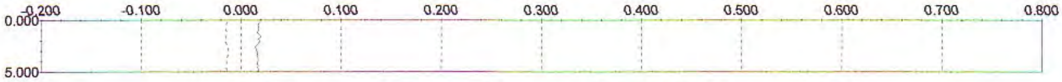

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  M                    0.5144  0.0170 -0.0141     0.5144         8/24/2011
Time                     User Name                 Device Name
11:43:35 AM(+0600)  System Administrator AA
6ppm-nt : UNK Average
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                  0.4917  0.0168 -0.0142 10        1.000000      1.00     1.00
CF              ActualConc.  Actual Conc. Unit %RSD       SD               C#  SG#
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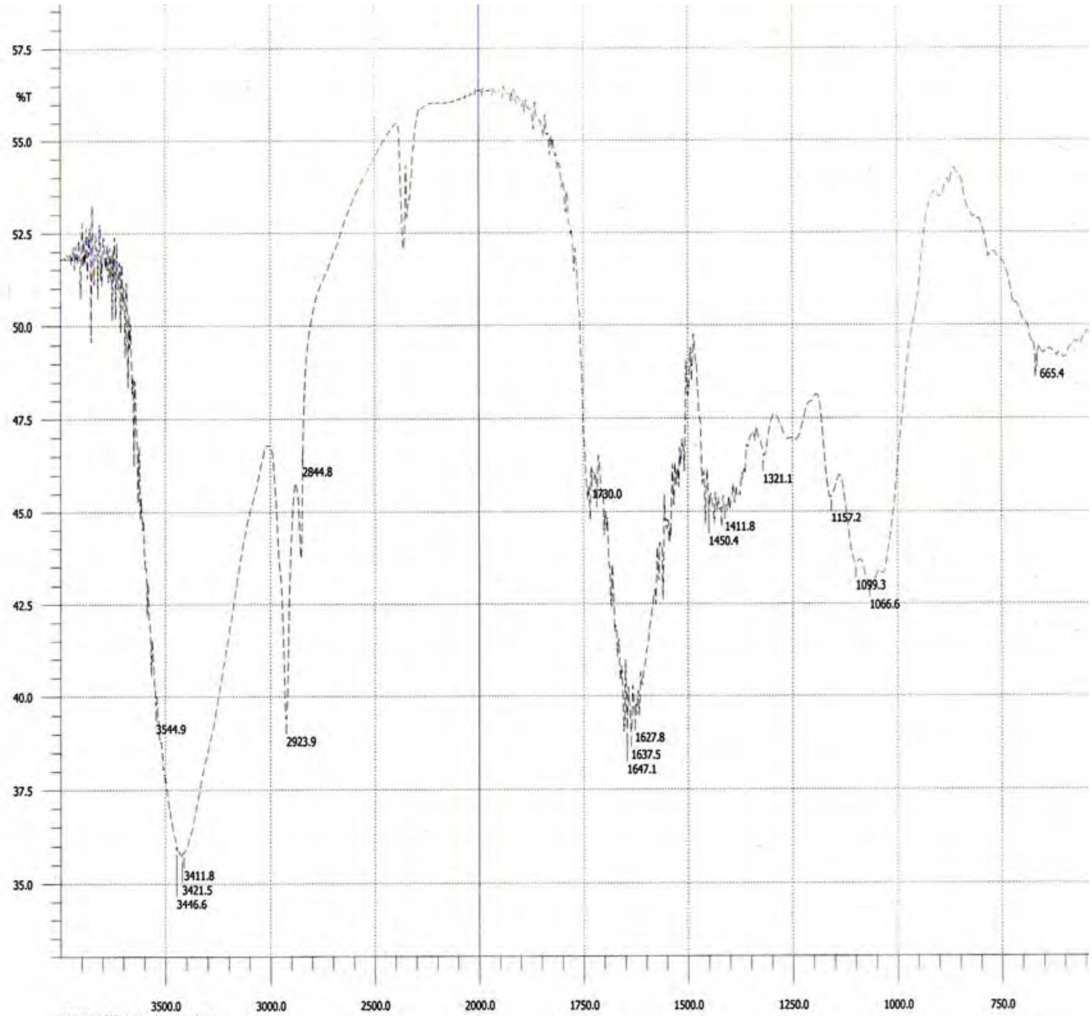
IR Spectrum of NLP Before Adsorption



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DEFAULT.IRS: NLP-1 June 14 .2011
Date:      01/01/1999  Time:           12:04:48   NScans:        45
Type:      HYPER IR    User:           user       Detector:      standard
Abscissa:  1/cm        Ordinate:       %T         Apodization:   Happ
Min:       401.17      Max:            3998.16    Range:         1/cm
Ndp:       1866        Data Interval:  1.92868    Resolution:    4.0
Gain:      auto        Aperture:       auto       Mirror Speed:  2.8(low)
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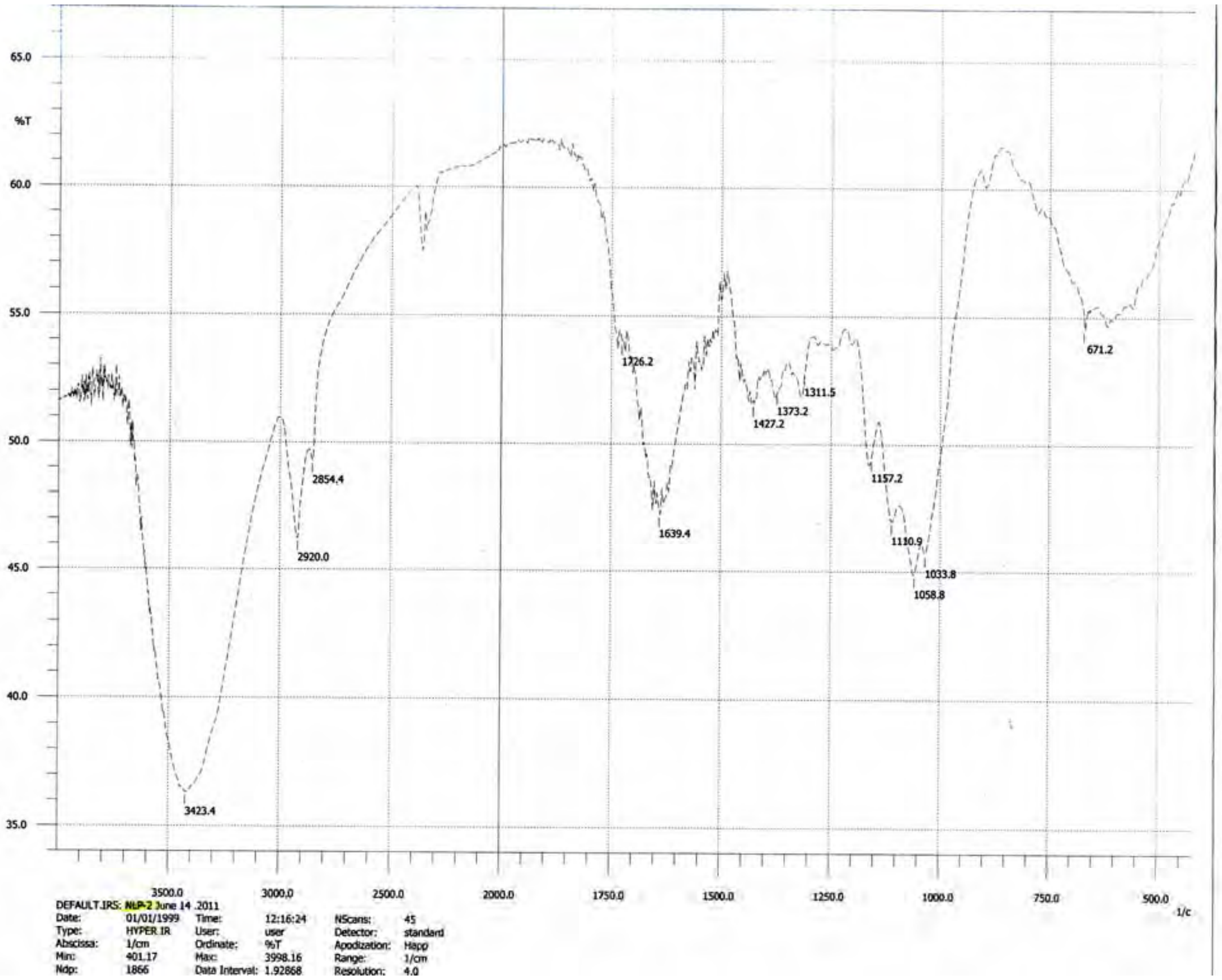
IR Spectrum of NLP After Adsorption of Cd(II)



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DEFAULT.IRS: NLP-2 June 14 .2011
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Type:       HYPER IR     User:           user       Detector:     standard
Abscissa:   1/cm         Ordinate:       %T         Apodization:  Happ
Min:        401.17       Max:            3998.16    Range:        1/cm
Ndp:        1866         Data Interval:  1.92868    Resolution:   4.0
```

4 Results and Discussion

4. 1 Adsorption of Metal ions from Prepared Standard Solution

4. 2 Adsorption of Metal ions from Industrial Effluent

4.1.1 Lead

4. 1. 1. 1 Effect of Contact Time and Initial Metal ion Concentration

The experimental results of adsorptions at various Pb(II) ion concentrations of 4.0, 6.0, 8.0 and 10.0 mg/L at different contact time were shown in Figures 5, 6 and 7, of NLP, NSP, and JSP, respectively. The equilibrium data reveal that, percent adsorption decreased with an increase in initial Pb(II) ion concentration, but the actual amount of Pb(II) ion adsorbed per unit mass of NLP, NSP and JSP increased with increase in Pb(II) ion concentration. It means that the adsorption is highly dependent on initial concentration of Pb(II) ions. It is because of the fact that at lower concentration, the ratio of the initial number of Pb(II) ion to the available surface area is low subsequently the fractional adsorption becomes independent of initial concentration. However, at high concentration the available sites of adsorption becomes fewer and hence the percentage removal of Pb(II) ions is dependent upon initial concentration [113]. It took five hours to reach equilibrium for all concentrations. Figures 5, 6 and 7 reveal that the curves are single, smooth, and continuous, leading to saturation, suggesting the possible monolayer coverage of the Pb(II) ions on the NLP, NSP and JSP surface.

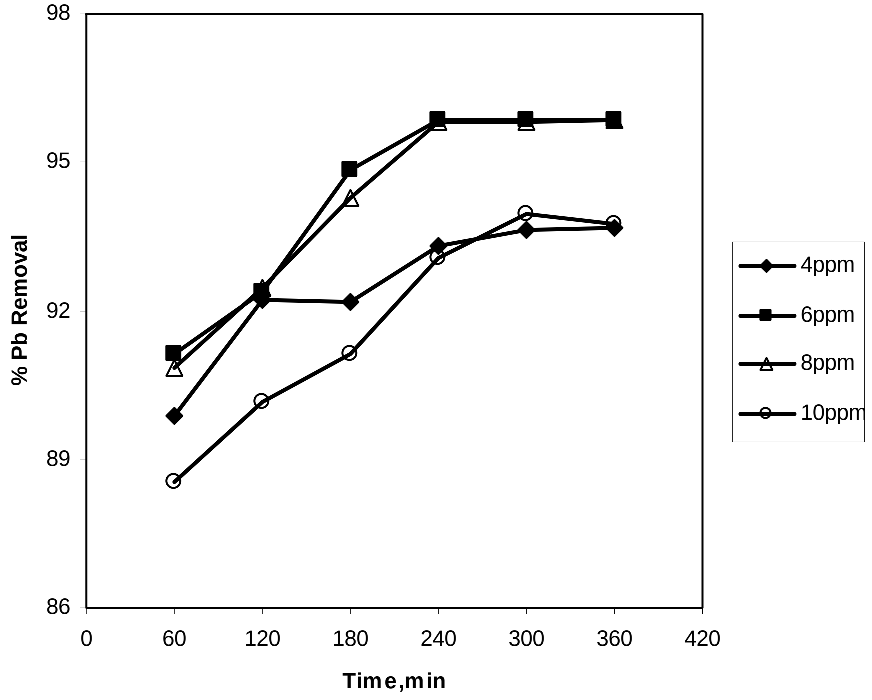

Figure 5: % of Pb(II) Removal vs Contact time with NLP

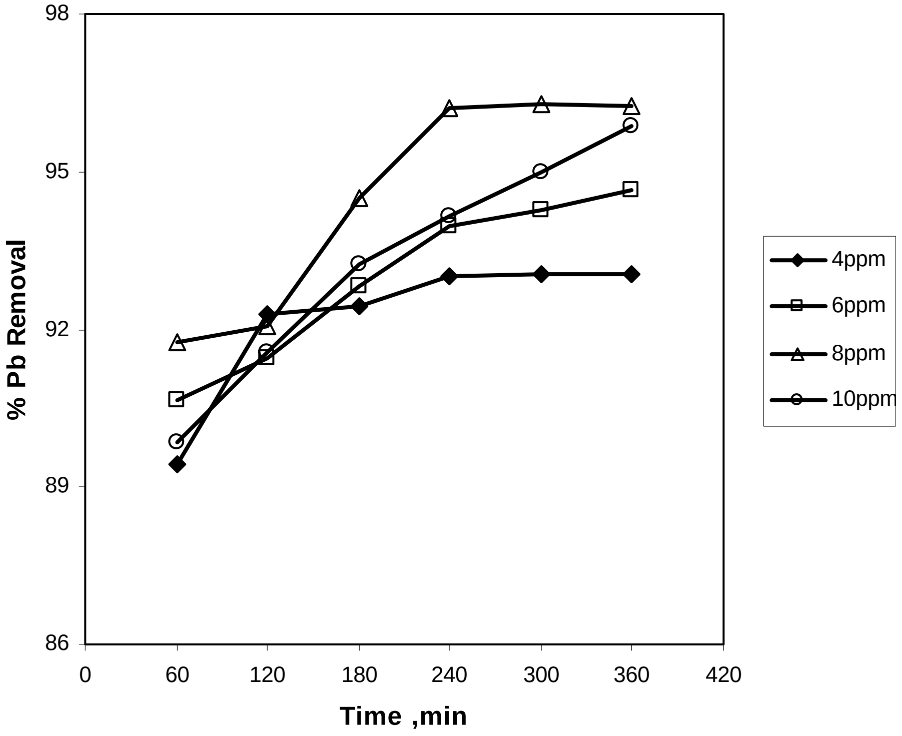

Figure 6: % of Pb(II) Removal vs Contact time with NSP

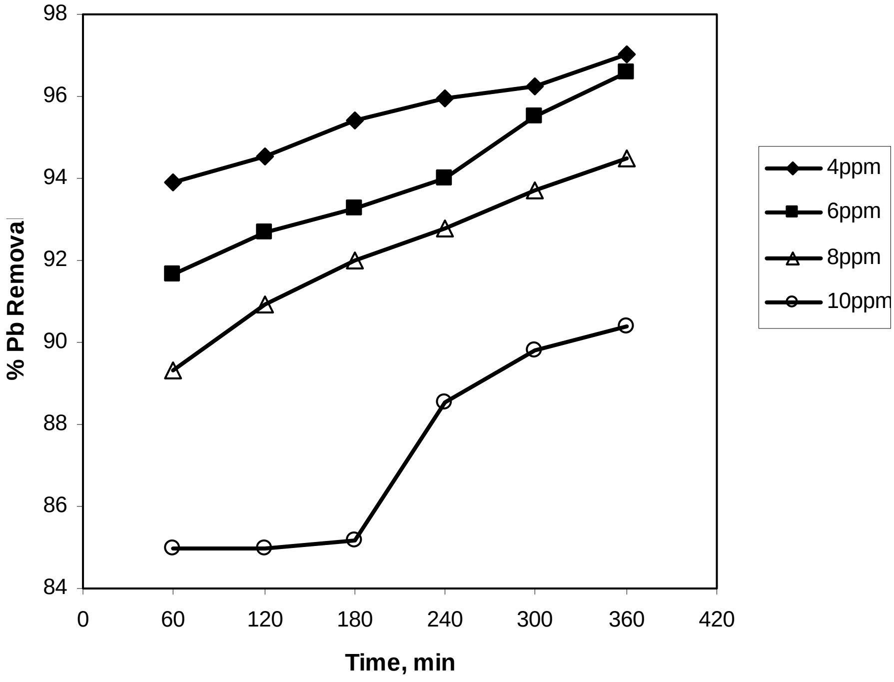

Figure 7: % of Pb(II) Removal vs Contact time with JSP

4. 1. 1. 2 Effect of Adsorbent Dosage

The effect of adsorbent dosage on the removal capacity was also studied for NLP, NSP and JSP. The removal capacity of Pb(II) ion was determined by passing Pb(II) solutions of different concentrations (4.0 mg/L- 10.0mg/L) through the column using a fixed amount (1g) of adsorbent. Secondly, the data were collected for varying amounts of the adsorbent (NLP) at a fixed concentration of (6.0 ppm) Pb(II) ion-solution. The Pb(II) ion concentration was then measured in the outlet to calculate the percent of removal as shown in Table 1. It was observed that 1g NLP adsorbed Pb(II) ion from 100 ml Pb(II) solution of 4.0 ppm, 6.0 ppm, 8.0 ppm and 10.0 ppm and percentage of adsorption were 93.64%, 96.27%, 95.83% and 93.96%, respectively. Similarly, NSP and JSP were studied and the data are given in Table 1.

The relation between the percentages of removal of Pb(II) with adsorbent dosage is shown in Figure 8. From this curve, it is clear that the percent of removal of Pb(II) increased with the increase of adsorbent dosage and reached almost saturation with 96.27%, 94.45% and 95.57% removal for NLP, NSP and JSP, respectively when the amount of adsorbent was ≥ 2g of adsorbents for the 6.0 ppm Pb(II) in 100mLsolution.

Table 1: Data for the fixed amount of adsorbent dosage of NLP, NSP and JSP equilibrium at 360 minutes

Amount Adsorbent (g)	Initial metal Conc., *Co* (ppm)	% of Pb Removal		
		NLP	NSP	JSP
1g	4	93.64	93.05	96.26
	6	96.27	94.27	95.50
	8	95.83	96.27	93.71
	10	93.96	95.00	89.81

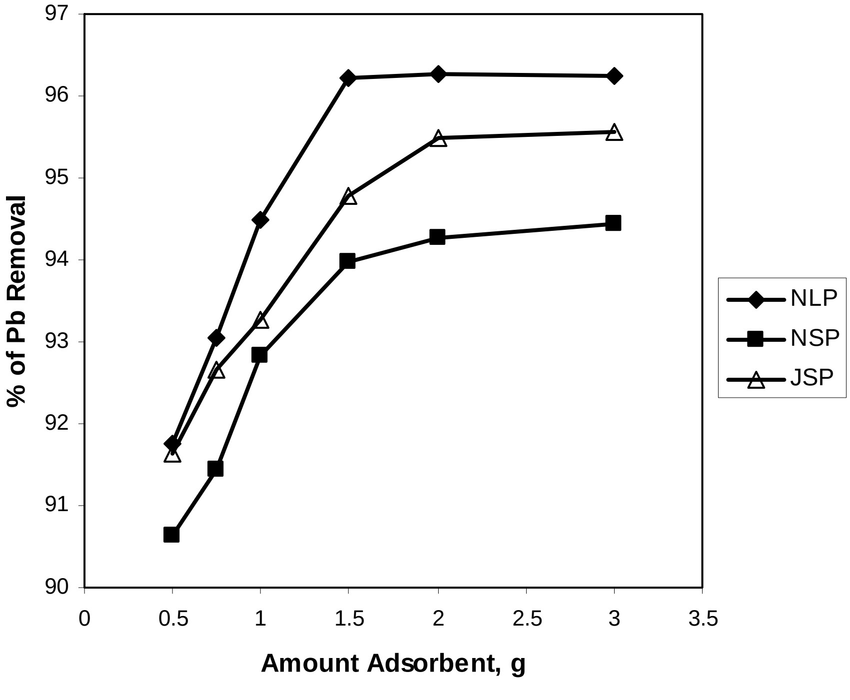

Figure 8: Effect of adsorbent dosage (NLP, NSP, and JSP) on the removal of Pb(II) with fixed concentrated solution (6.0 mg/L) and contact time 360 minutes

4.1.1. 3 Evaluation of Bio-sorption Efficiency

Sequestering of metallic species by biomass has been traced mainly into the cell wall of the fungal biomass. The cell wall is not necessarily the only site where the sequestered metals might be situated. They may also be found within the cell, coupled with various organic parts or may crystallize in the cytoplasm [114] or may interact with DNA and RNA. The drying and then grinding of bio-adsorbent, following heating at around 65ºC unveiled the sites where metal ion could be sequestered, increasing the probability of encountering metal ions at such sites [115].

The biosorption data for the removal of Pb(II) ions were correlated with Langmuir and Freundlich models [116]. The Langmuir equation (Eq.1) is valid for monolayer sorption on a surface containing a limited number of sites, predicting a homogeneous distribution of sorption energies.

Using the Langmuir equation (Eq.1), the linear plots of $1/C_{ads}$ versus $1/Ce$ were obtained which suggest the applicability of the Langmuir isotherm was shown in Figures 9, 10 and 11 for NLP, NSP and JSP, respectively. Values of K_L and b were determined from slope, $1/K_Lb$ and intercept $1/K_L$ of the plots and were presented in Table 2.

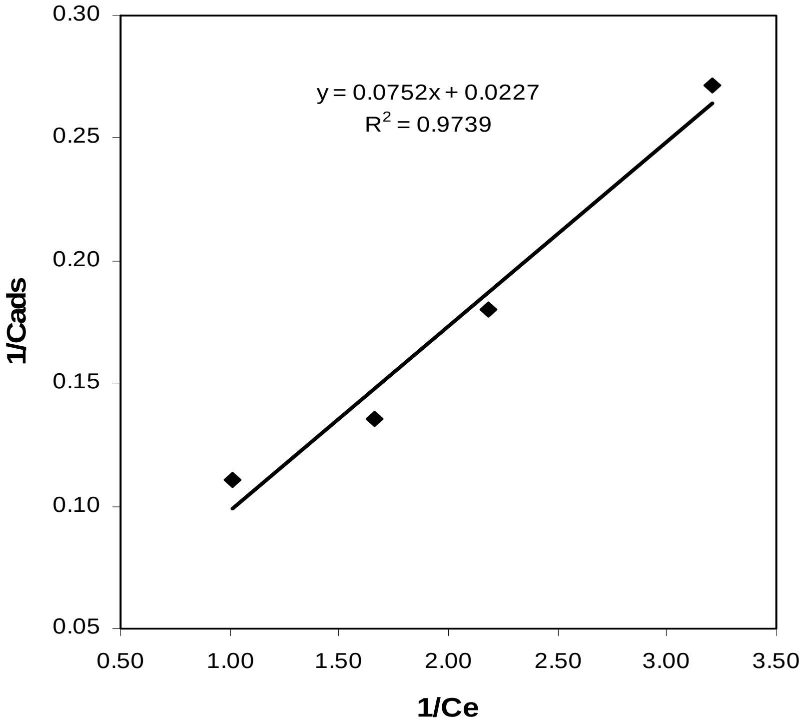

Figure 9: Langmuir isotherm model for adsorption of Pb(II) ion onto NLP.

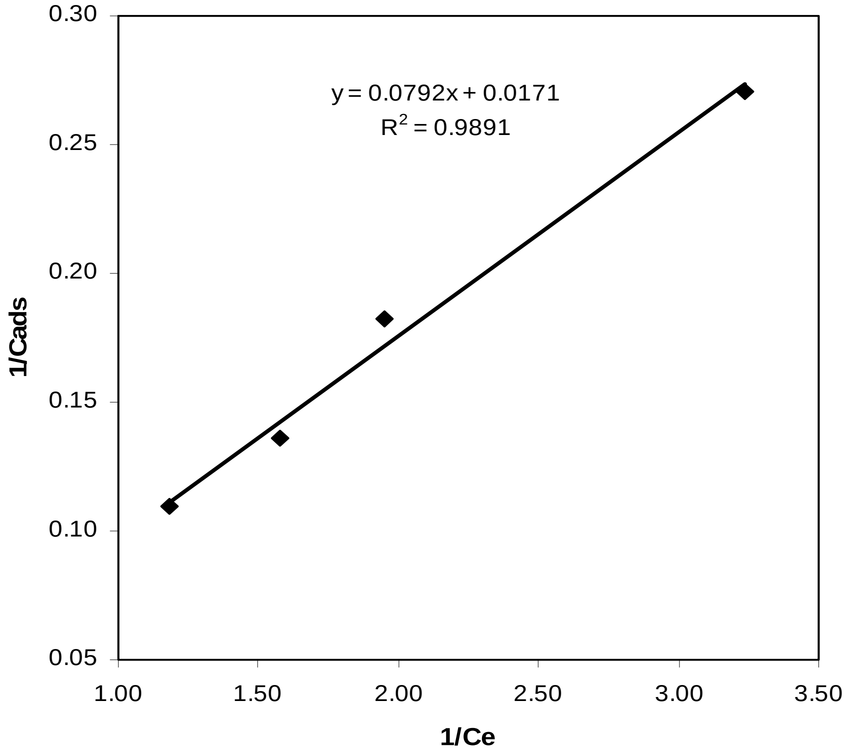

Figure 10: Langmuir isotherm model for adsorption of Pb(II) ion onto NSP.

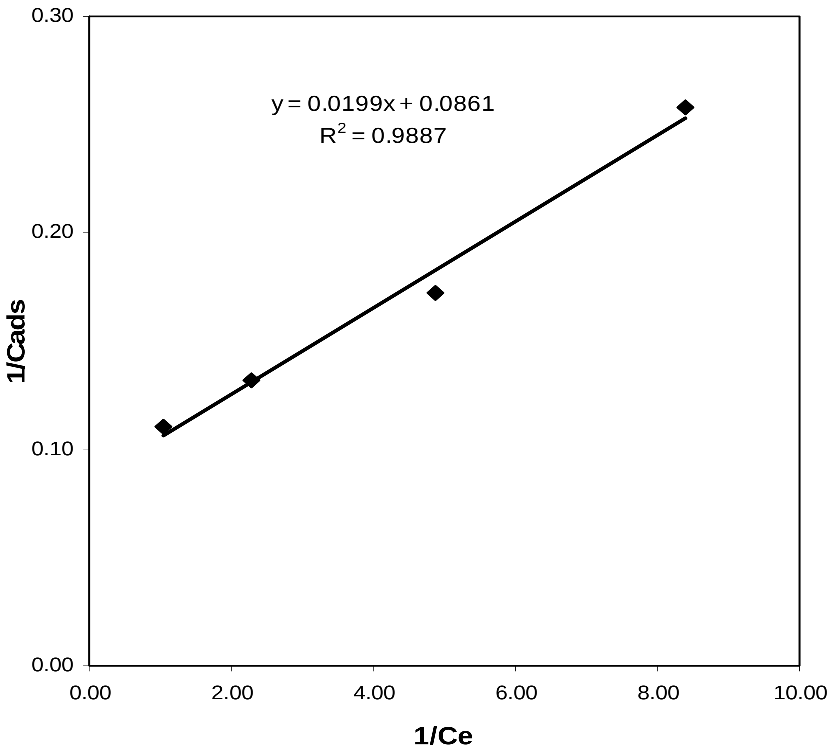

Figure 11: Langmuir isotherm model for adsorption of Pb(II) ion onto JSP.

Table 2: Langmuir constants for adsorption of Pb(II) ion onto NLP, NSP, JSP.

Langmuir Constants			
Different Adsorbents	K_L kg/kg (Pb(II)/Ads)	*b* m^3 /kg	R^2
NLP	4.405×10^{-3}	302	0.9739
NSP	5.848×10^{-3}	216	0.9891
JSP	1.161×10^{-3}	4327	0.9887

The observed K_L values suggest that the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on adsorbent surface with constant energy and no transmission of adsorbate in the plane of the adsorbent surface. The observed *b* values shows that the adsorbent prefers to bind acidic ions and that speciation predominates on sorbent characteristics, when ion exchange is the predominant mechanism takes place in the adsorption of Pb(II) ion.

Further, the essential features of the Langmuir adsorption isotherm can be expressed in terms of dimensionless constant, called separation factor or equilibrium parameter (R_L) which can be defined as follows:

$$R_L = \frac{1}{1 + bC_0} - - - - - - - (5)$$

where, C_o is the initial concentration of the adsorbate i.e. metal ion. The significance of equation 5 is that, when $R_L > 1$, the adsorption is unfavorable; when $0 < R_L < 1$, the adsorption is favorable and when $R_L = 0$, the adsorption is irreversible. According to Ganjidoust et al**.** [117], the adsorption is favorable since the obtained values of R_L are in the range of zero to one. The R_L values of different adsorbents are shown in Table 3.

Table 3: R_L Values derived from experimental data

Adsorbent Name	Dimensionless factor, R_L range
NLP	0.249 – 0.453
NSP	0.316 – 0.536
JSP	0.023 – 0.055

The Freundlich equation (Eq.2) was also employed for the adsorption of Pb(II) ions on different adsorbent. The constants K_f and $1/n$ are incorporating all factors affecting the adsorption capacity and intensity of adsorption, respectively. Linear plots of log C_{ads} versus log Ce showed the adsorption of Pb(II) ions with different adsorbent of the Freundlich isotherm (Figures 12, 13 and 14).

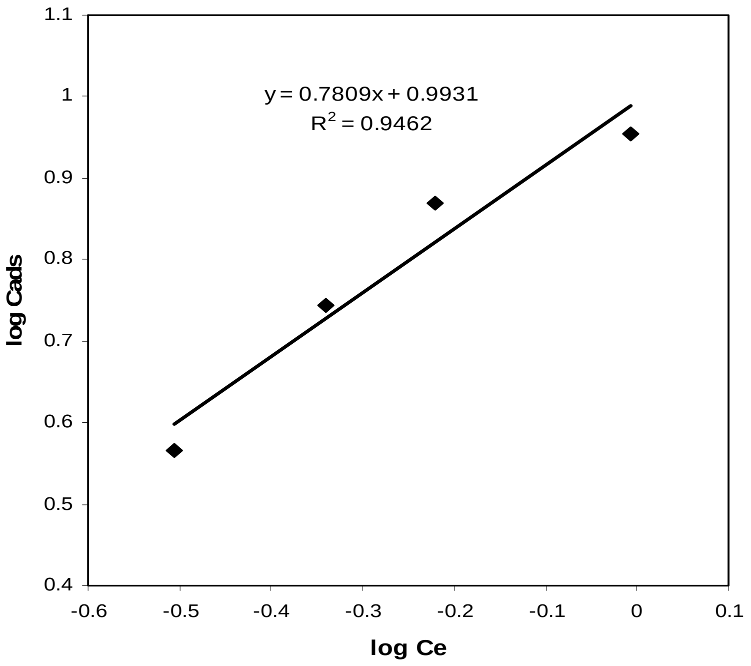

Figure 12: Freundlich isotherm model for adsorption of Pb(II) ion onto NLP

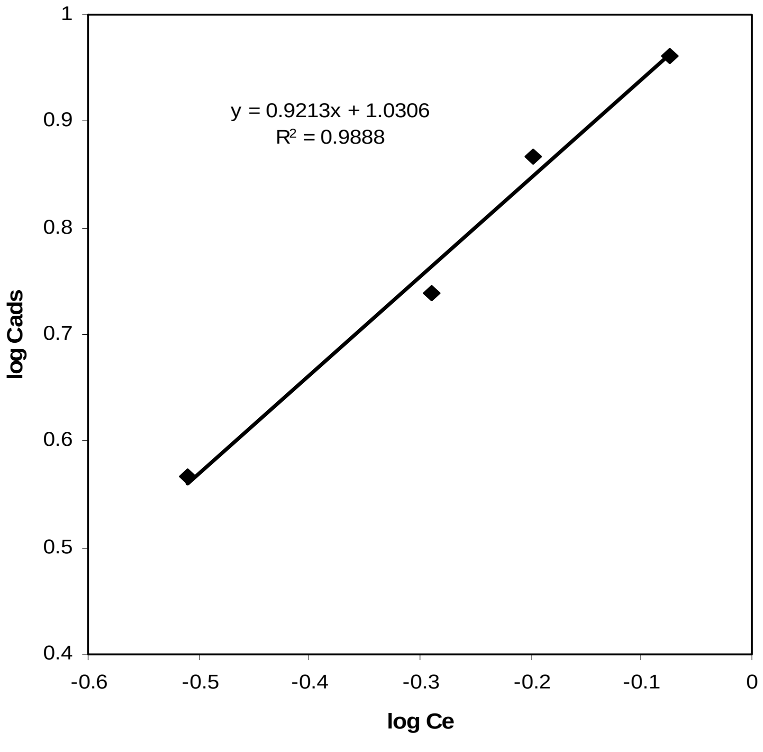

Figure 13: Freundlich isotherm model for adsorption of Pb(II) ion onto NSP

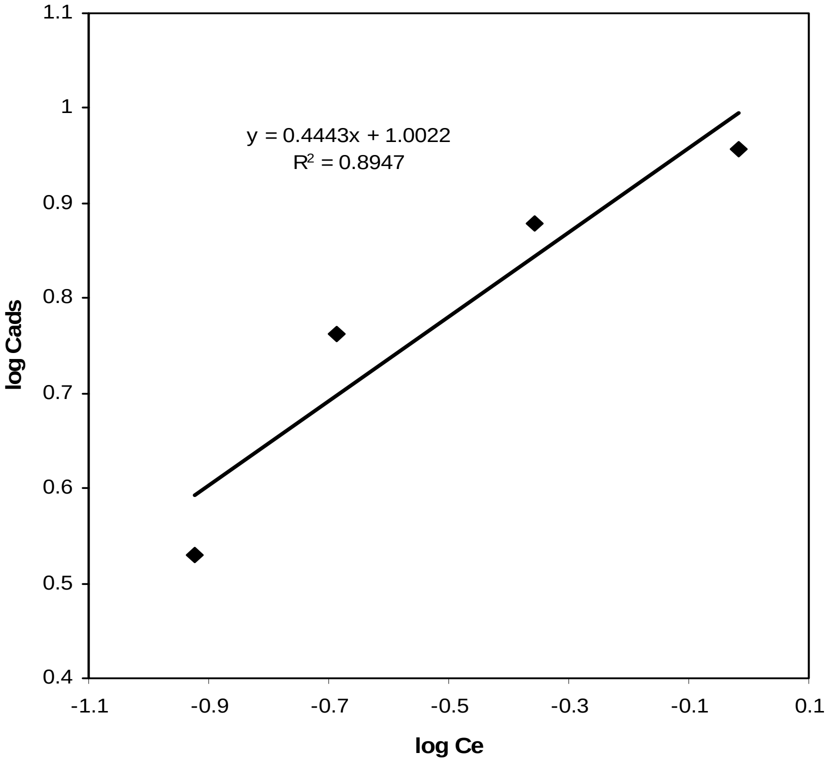

Figure 14: Freundlich isotherm model for adsorption of Pb(II) ion onto JSP

Table 4: Freundlich Isotherm constants derived from the adsorption of Pb(II) ion on NLP, NSP and JSP

Freundlich Constants			
Adsorbent Name	K_f kg/kg (Pb/Ads)	n kg/m^3	R^2
NLP	0.984×10^{-3}	1.281	0.9462
NSP	1.073×10^{-3}	1.085	0.9888
JSP	1.005×10^{-3}	2.251	0.8947

If $1/n < 1$, bond energies increase with surface density, if $1/n > 1$, bond energies decrease with surface density and if $1/n = 1$ all surface sites are equivalent [118]. By plotting log C_{ads} vs log C_e, a straight line was obtained as shown for NLP, NSP and JSP in Figures 12, 13 and 14, respectively. From the slope and intercept of the Figures 12, 13 and 14; the constants $1/n$ and K_f were found to be 0.7809, 0.9213, 0.4443 and 0.984×10^{-3}, 1.073×10^{-3}, 1.005×10^{-3}, respectively. This behavior shows that the adsorption also follows the Freundlich isotherm, i.e. the adsorption is favorable. The values of Kf, n and R^2 for the NLP, NSP, JSP adsorbent were listed in Table 4.

The observed values of K_f and n shown in the Table 4 reveal that the increase in negative charges on the adsorbent surface, that favors adsorption through electrostatic force like Van der Waal's between the adsorbent surface and Pb(II) ion. The higher atomic weight, large size and radii of the Pb(II) ions have limits the possibility of the adsorption of Pb(II) ion onto adsorbent in higher concentration. However, the values clearly show the dominance in adsorption capacity. The values of n are greater than one indicating the adsorption is much more favorable.

The values of equilibrium constant of adsorption of Pb(II) ion onto NLP, NSP and JSP are related to the free energy of adsorption as follows [119],

$$K_0 = \frac{C_{solid}}{C_{liquid}}$$

$$\text{Or, } \Delta G^0{}_{ads} = -2.0303RT\log K_0 ------(6)$$

where K_o is the equilibrium constant, C_{solid} is the solid phase concentration at equilibrium (mg/ L), C_{liquid} is the liquid phase concentration at equilibrium (mg/L), $\Delta G^o{}_{ads}$ is the free energy of adsorption, R is the gas constant, T is the absolute temperature. Values of $\Delta G^o{}_{ads}$ calculated from equation 6 were recorded in Table 5. The results indicated that values of free energy are less negative than the threshold value required for chemical adsorption hence the adsorption of Pb(II) ion onto NLP, NSP and JSP are spontaneous and is consistent with the mechanism of physical adsorption. This is further confirmed from the analysis of IR spectra of the adsorbent before and after adsorption of metal ion. No significance changes in the stretching modes were observed. (Specimen IR, spectra are shown in page 65 and 66). This indicates that no bond formation between the adsorbent and adsorbate.

Table 5: Adsorption data for Pb(II) on NLP, NSP, and JSP and Free Energy.

Initial Conc. C_o (mg/L)	Equilibrium Conc. C_e (mg/L)			Amount Adsorbed C_{ads} (mg/g)			ΔG^o_{ads} (kJ/mol)		
	NLP	NSP	JSP	NLP	NSP	JSP	NLP	NSP	JSP
4.0	0.312	0.309	0.119	3.688	3.691	3.881	–6.122	–6.149	–8.631
6.0	0.458	0.513	0.206	5.542	5.487	5.794	–6.181	–5.872	–8.273
8.0	0.602	0.635	0.440	7.398	7.365	7.560	–6.216	–6.073	–7.049
10.0	0.985	0.843	0.963	9.015	9.157	9.037	–5.488	–5.910	–5.548

4.1.1.4 Effect of pH

The experiments carried out at different initial pH show that the adsorption percentage increases with increase in initial pH of the medium up to 7 and then decreases as depicted in the Figure 15. This behavior can be explained using pH of the adsorbent. In addition the decrease in adsorption of metal ions at low pH can be attributed to the competition between H^+ and metal ions. It is thus clear from Figure 15 that at lower pH, the adsorption of Pb(II) ion studied is drastically reduced. This observation was made to use of to desorb the Pb(II) ion from the adsorbed material.

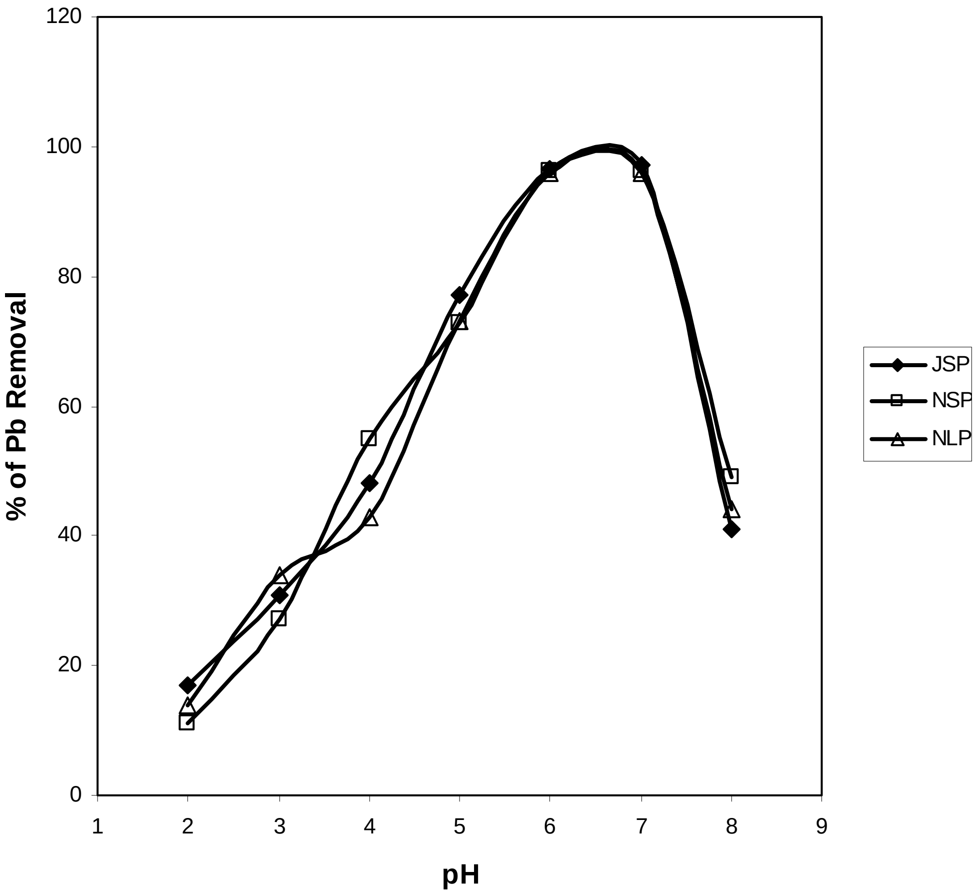

Figure 15: Effect of pH for removal of Pb(II) ion onto NLP, NSP, JSP, contact time 360 minutes, Pb(II) ion 6.0 mg/L and adsorbent 1.0 g.

4.1.1.5 Desorption Studies

In metal ion removal process, it is important to study desorption of the adsorbed metal ions under suitable conditions. In the desorption studies deionized water was used as a desorbing agent. The NLP, NSP and JSP samples loaded with different adsorbed amount of Pb(II) ions (initial Pb(II) concentration are 4.0, 6.0, 8.0 and 10.0 mg/L) were placed in 100 ml deionized water and the amount of Pb(II) ions desorbed were measured from 0.5 g of different adsorbents after two hours contacted time. Table 6 shows the data of the adsorbed and desorbed amount of Pb(II).ions. The data showed that there was small amount Pb(II) ions desorbed from different adsorbent surface indicating the strong contact between Pb(II) ion and NLP, NSP and JSP surfaces.

But when we use 0.1M HCl as a desorbing agents, the percentage of desorption is higher. The desorption indicate that hydrochloric acid is a better reagent for desorption of Pb(II) ion from NLP, NSP and JSP. The reversibility of adsorbed Pb(II) ions in mineral acid or base is in agreement with the pH dependent results obtained. The desorption of Pb(II) ions by mineral acid medium indicates that the Pb(II) ions were adsorbed onto the NLP, NSP and JSP through by physisorption mechanisms.

Table 6: Adsorption and Desorption data for Pb(II) on NLP, NSP, and JSP

Initial Conc. C_o (mg/L)	Amount Adsorbed, C_{ads} (mg/g)			% Desorption with deionized water			% Desorption with 0.1M HCl		
	NLP	NSP	JSP	NLP	NSP	JSP	NLP	NSP	JSP
4	3.688	3.691	3.881	0.050	0.056	0.052	2.356	1.019	1.763
6	5.542	5.487	5.794	0.064	0.051	0.057	2.012	1.243	1.080
8	7.398	7.365	7.560	0.061	0.066	0.063	3.079	2.064	1.983
10	9.015	9.157	9.037	0.043	0.065	0.065	2.874	1.704	2.045

4. 1.1. 6. Adsorption Kinetics

The study of adsorption kinetics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface. The adsorption behaviour of Pb(II) ions onto NLP, NSP and JSP was analyzed using pseudo first-order and pseudo second-order kinetic models. The conformity between experimental data and the model predicted values is expressed by the correlation coefficients (R^2, values close or equal to 1). A relatively high R^2 value indicates that the model successfully describes the second order kinetics of metal ions adsorption onto the adsorbents.

The Pseudo First-order Equation

Applying the pseudo first-order equation, (Eq.3) (Lagergren equation) for NSP, NLP and JSP we obtain the Figures 16, 17 and 18, respectively.

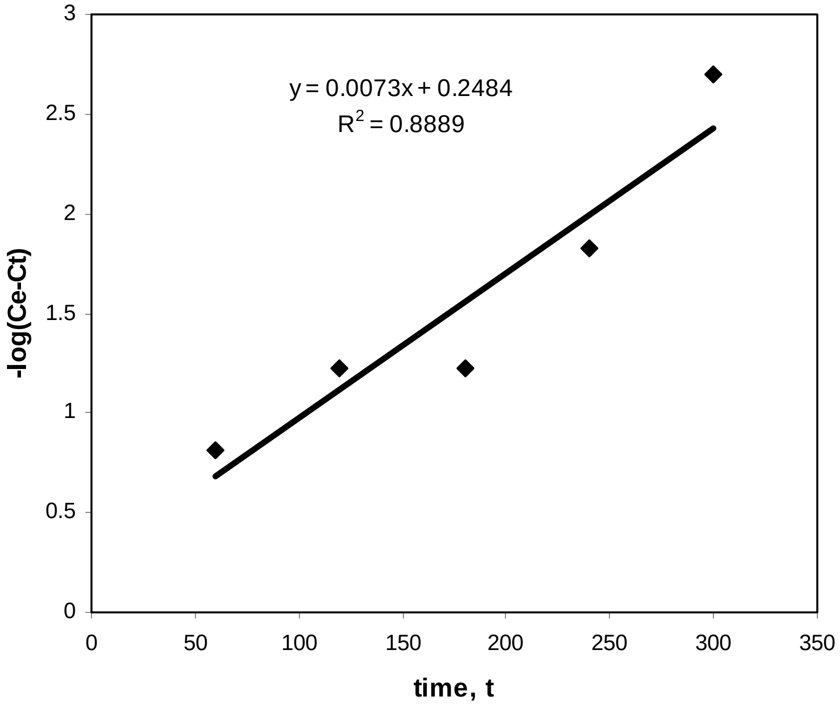

Figure16: –log ($C_e - C_t$) vs *t* for removal of Pb(II) onto NLP, Equilibrium time 360 minutes, Pb(II) ion Conc. 4.0 mg/L and adsorbent 1.0 g.

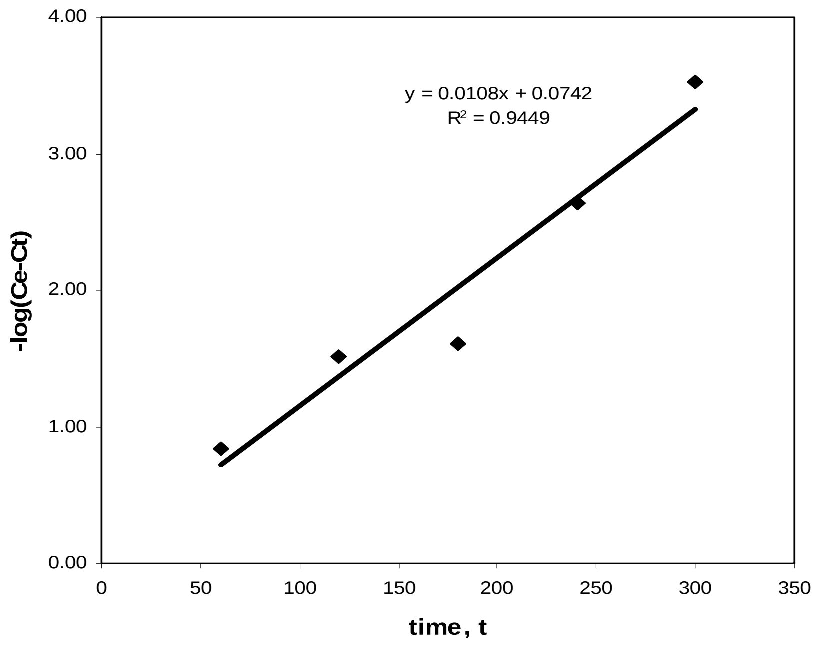

Figure 17: –log ($C_e - C_t$) vs t for removal of Pb(II) onto NSP, Equilibrium time 360 minutes, Pb(II) ion Conc. 4.0 mg/L and adsorbent 1.0 g.

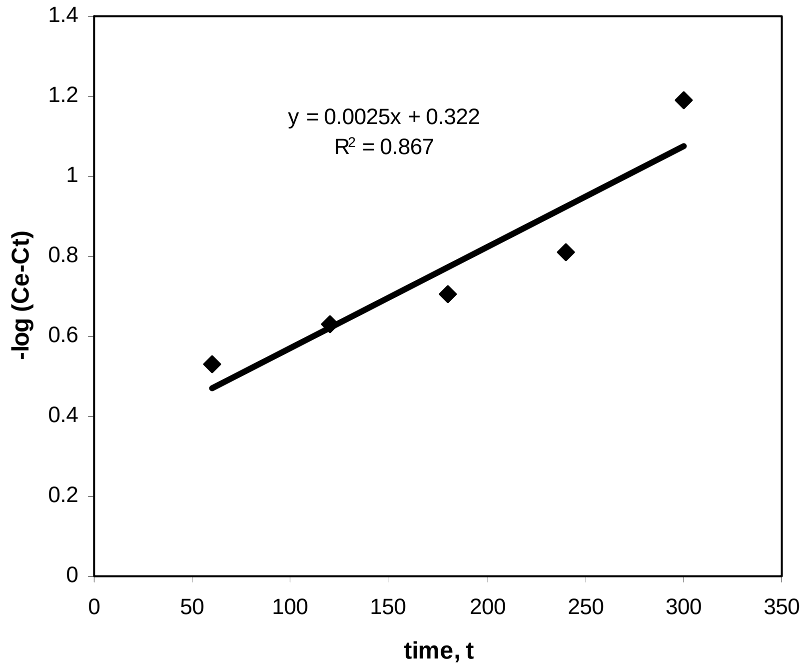

Figure 18: –log ($C_e - C_t$) vs t for removal of Pb(II) onto JSP, Equilibrium time 360 minutes, Pb(II) ion Conc. 4.0 mg/L and adsorbent 1.0 g.

The value of log ($C_e - C_t$) is linearly correlated with t. The plot of log ($C_e - C_t$) vs t should give a linear relationship from which k_1 and C_e were determined from the slope and intercept of the plot, respectively and the values are shown in Table 7.

Table 7: The adsorption kinetic constants for Pb (II) ion on NLP, NSP and JSP

Adsorbent	Pseudo first order		Pseudo second order		
	k_1	R^2	k_2 ($g.mg^{-1}.min^{-1}$)	h ($mg.g^{-1}.min^{-1}$)	R^2
NLP	0.0168	0.8889	0.7654	0.1096	1
NSP	0.0249	0.9449	1.0940	0.1539	1
JSP	0.0058	0.8670	0.2731	0.0935	0.9996

The Pseudo Second-order Equation

From the pseudo second-order adsorption kinetic rate equation (Eq.4), we were plotted (t/C_t) vs t for Pb(II) ions onto different adsorbent (Figures 19, 20 and 21 for NSP, NLP and JSP, respectively) and the plot show a linear relationship. C_e and k_2 can be determined from the slope and intercept of the plot, respectively and listed in Table 7.

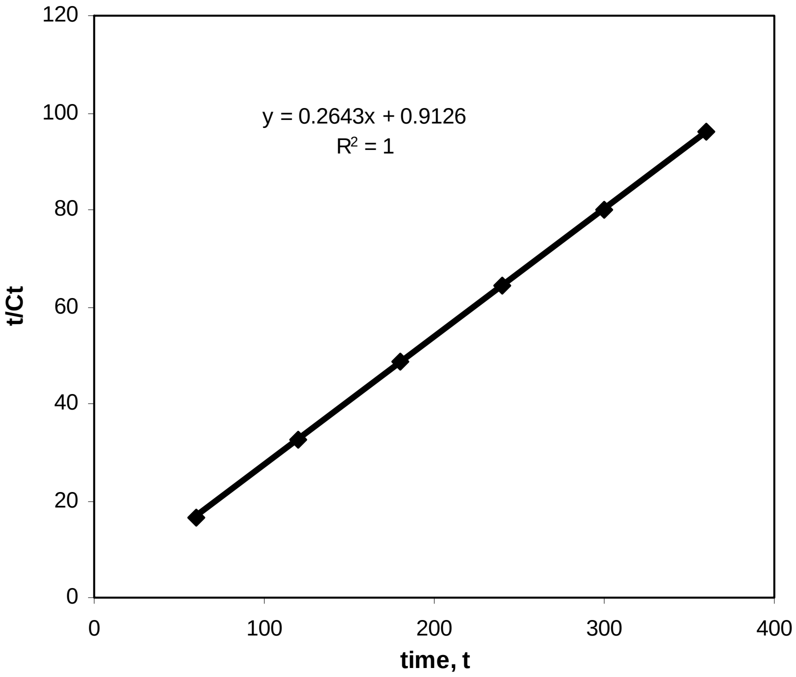

Figure 19: *(t/Ct) vs t* for removal of Pb(II) onto NLP, Equilibrium time 360 minutes, Pb(II) ion Conc. 4.0 mg/L and adsorbent 1.0 g.

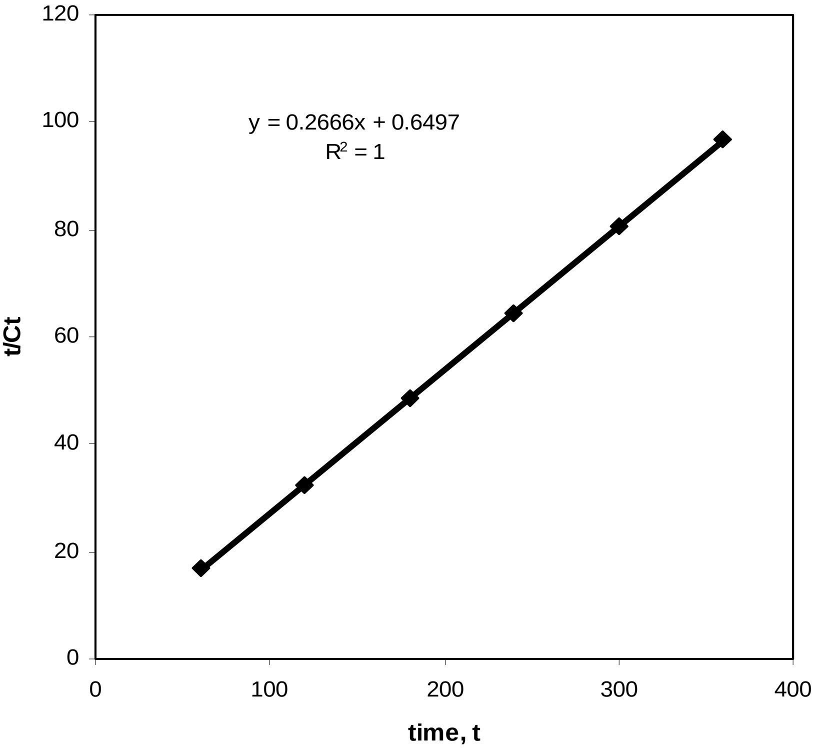

Figure 20: *(t/Ct) vs t* for removal of Pb(II) onto NSP, Equilibrium time 360 minutes, Pb(II) ion Conc. 4.0 mg/L and adsorbent 1.0 g.

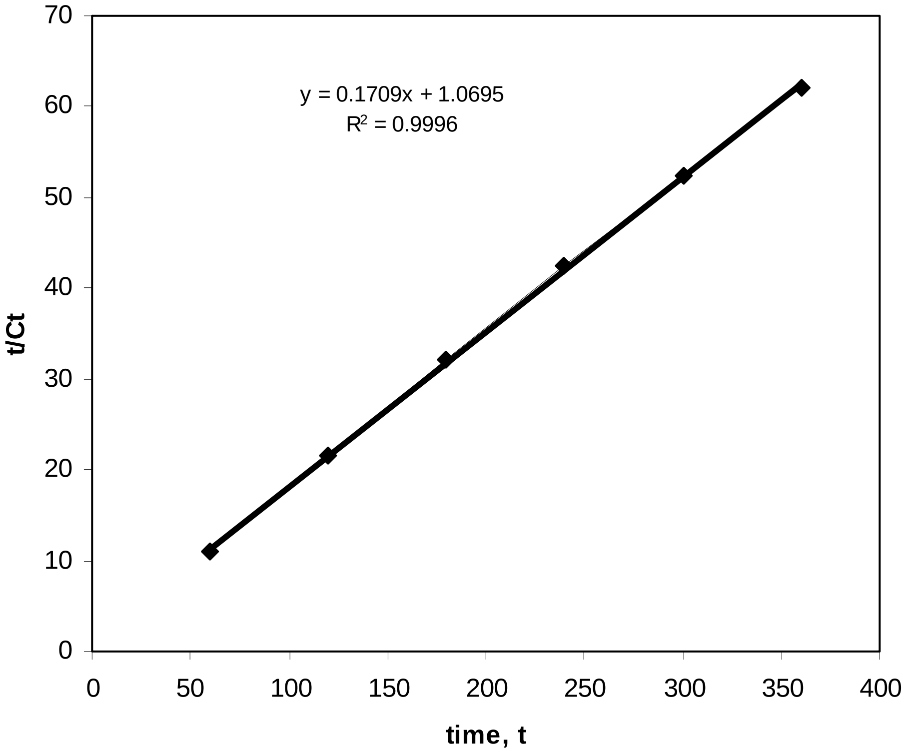

Figure 21: *(t/Ct) vs t* for removal of Pb(II) onto JSP, Equilibrium time 360 minutes, Pb(II) ion Conc. 4.0 mg/L and adsorbent 1.0 g.

4. 1. 2. Cadmium

4.1.2.1 Effect of Contact Time and Initial Metal ion Concentration

The experimental results of adsorptions at various Cd(II) ion concentrations 4.0, 6.0, 8.0 and 10.0 mg/L with contact time were shown in Figures 22, 23 and 24**.** The equilibrium data reveal that, percent adsorption decreased with an increase in initial Cd(II) ion concentration, but the actual amount of Cd(II) ion adsorbed per unit mass of NLP, NSP and JSP increased with an increase in Cd(II) ion concentration. It means that the adsorption is highly dependent on initial concentration of Cd(II) ion. Because at lower concentration, the ratio of the initial number of cadmium ion to the available surface area is low subsequently the fractional adsorption becomes independent of initial concentration. However, at high concentration the available sites of adsorption becomes fewer and hence the percentage removal of Cd(II) ions is dependent upon initial concentration [113]. It takes about five hours to establish equilibrium for all the adsorbents. Figures 22, 23 and 24 reveal that the curves are single, smooth, and continuous, leading to saturation, suggesting the possible monolayer coverage of the cadmium ion on the NLP surface.

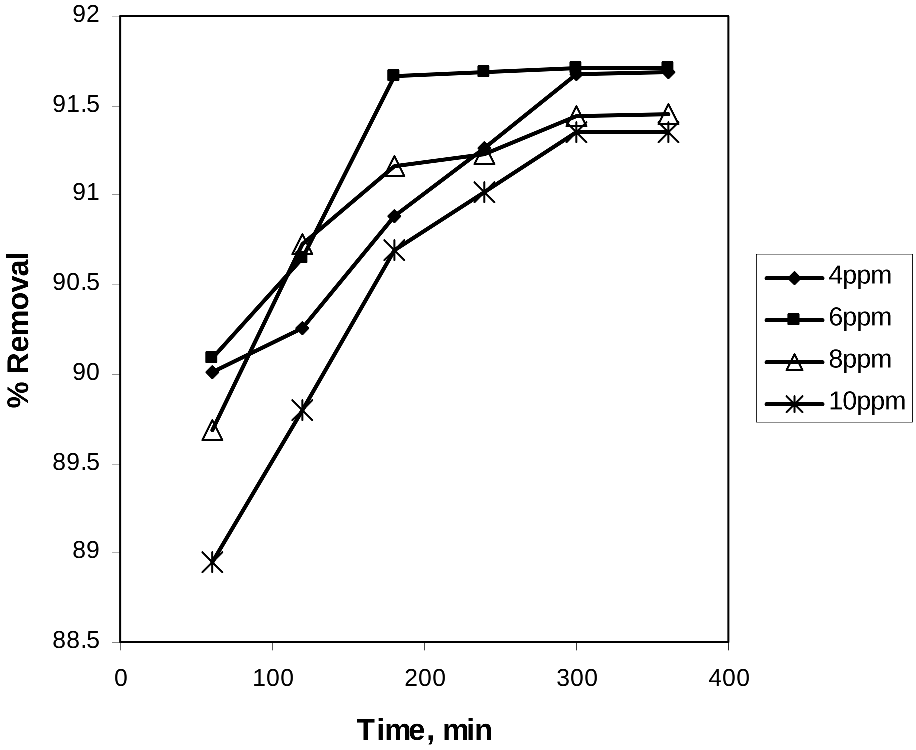

Figure 22: % of Cd(II) Removal vs Contact time with NLP

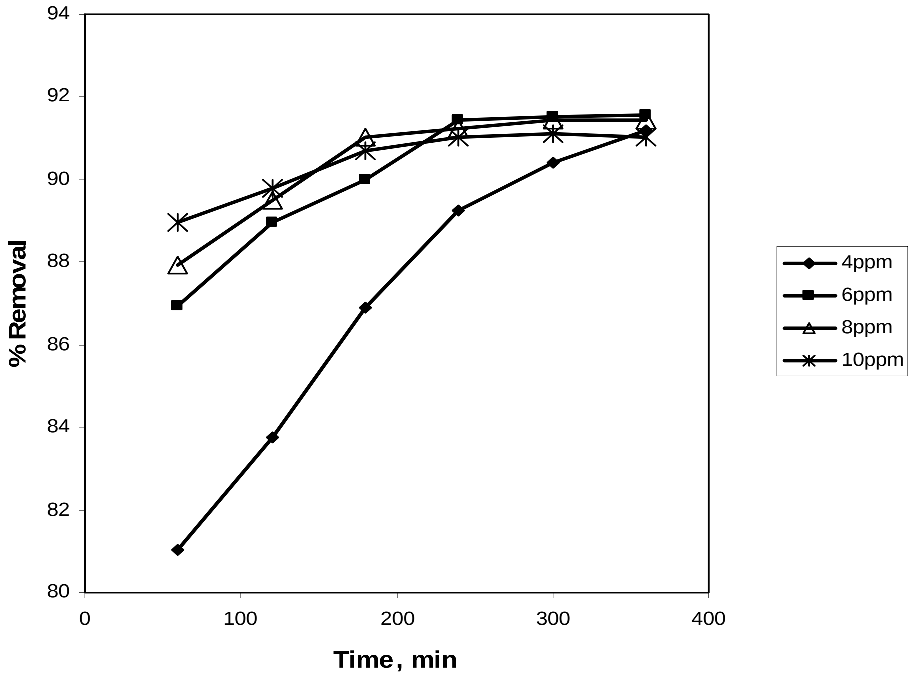

Figure 23: % of Cd(II) Removal vs Contact time with NSP

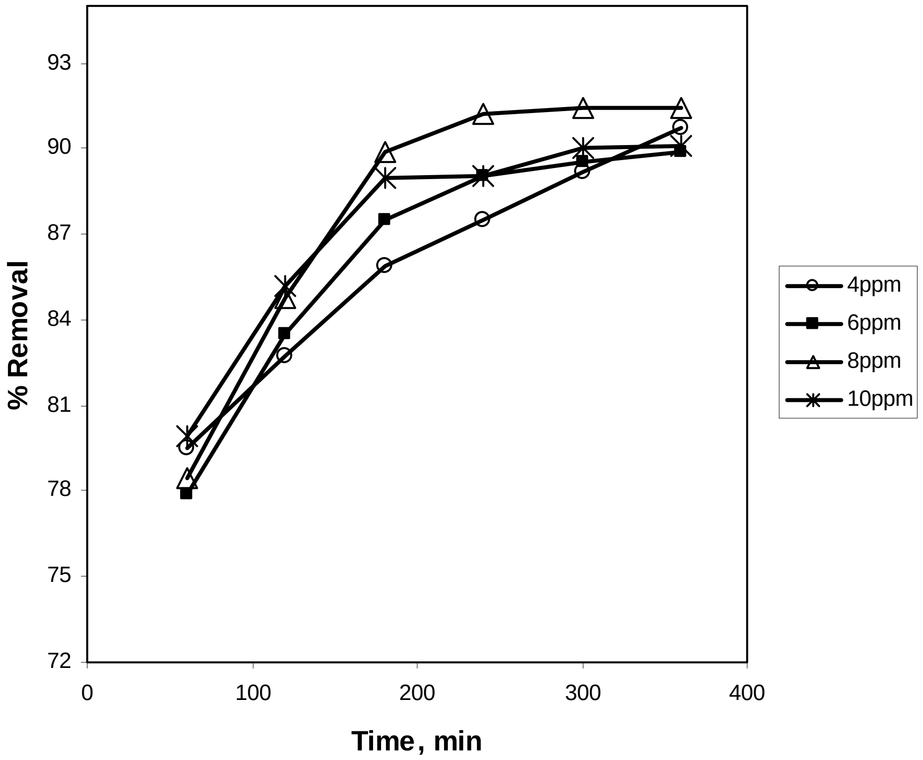

Figure 24: % of Cd(II) Removal vs Contact time with JSP

4.1.2.2 Effect of Adsorbent Dosage

The effect of adsorbent dosage on the removal capacity was also studied for NLP. For NLP, the removal capacity of Cd(II) ion was determined by passing different concentrated Cadmium(II) solutions (4.0 mg/L- 10.0mg/L) through the column using a fixed amount (1g) of adsorbent. Secondly, the data were collected for varying amounts of the adsorbent (NLP) at a fixed concentration of (6.0 ppm) Cd(II) ion-solution. The cadmium ion concentration was measured in the outlet to calculate the percent of removal shown in Table 7. It was observed that 1g NLP powder adsorbed cadmium ion from 100 ml cadmium solution of 4.0 ppm, 6.0 ppm, 8.0 ppm and 10.0 ppm and percentage of adsorption were 91.69%, 91.71%, 91.45% and 91.35%, respectively.

Table 8: Data for the fixed amount of adsorbent dosage of NLP equilibrium at 300 minutes

Amount Adsorbed (g)	Initial Conc. C_o (ppm)	Equilb. Conc. C_e (ppm)	% of Removal
1 g	4.0	0.3328	91.69
	6.0	0.4974	91.71
	8.0	0.6845	91.45
	10.0	0.8651	91.35

The relation between the percentages of removal of Cd(II) with adsorbent dosage is shown in Figure 25. It is clear from the figure that the percent of removal of cadmium increased with the increase of adsorbent dosage and reached almost saturation (96.16%), when the amount of the adsorbent is ≥ 2 g for the 6.0 ppm Cd(II) in 100ml solution.

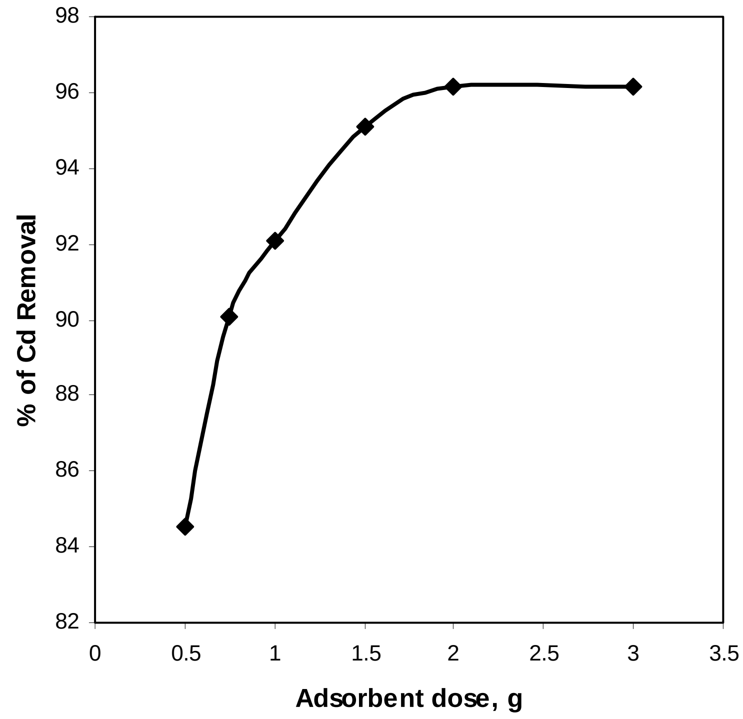

Figure 25: Effect of adsorbent dosage (NLP) on the removal of Cd(II) with fixed concentrated solution (6.0 mg/L) and contact time 360 minutes

4.1.2. 3 Evaluation of Bio-sorption Efficiency

The biosorption data for the removal of cadmium was correlated with Langmuir and Freundlich models [116]. The Langmuir equation (Eq.1), which is valid for monolayer sorption on a surface containing a limited number of sites, predicting a homogeneous distribution of sorption energies, is applying for different adsorbent.

The linear plots of $1/C_e$ versus $1/C_{ads}$ suggest the applicability of the Langmuir isotherm was shown in Figures 26, 27 and 28. Values of K_L and b were determined from slope and intercepts of the plots and are presented in Table 9.

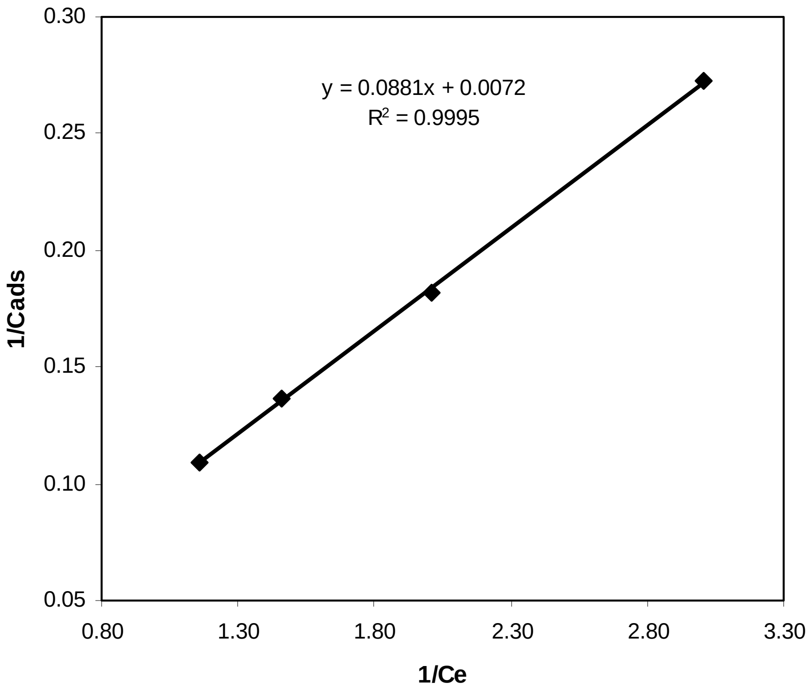

Figure 26: Langmuir isotherm model for adsorption of Cd(II) on NLP

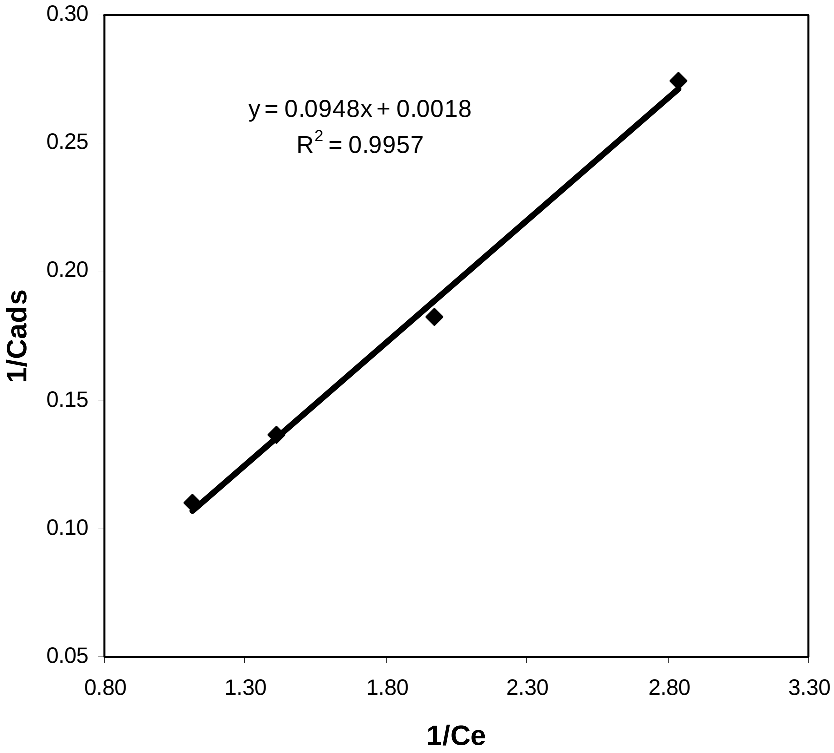

Figure 27: Langmuir isotherm model for adsorption of Cd(II) on NSP

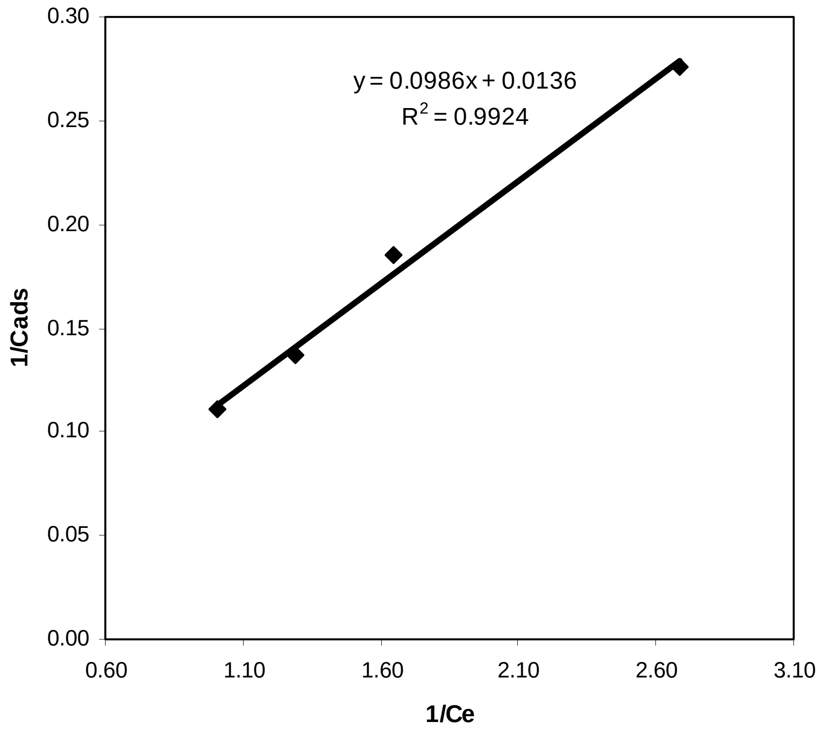

Figure 28: Langmuir isotherm model for adsorption of Cd(II) on JSP

Table 9: Langmuir and Freundlich constants derived from the adsorption of Cd(II) on NLP, NSP and JSP.

Adsorbent	Langmuir Constants			Freundlich Constants		
	K_L kg/kg (Cd/Ads)	b m^3 /kg	R^2	K_f kg/kg (Cd/Ads)	n kg/m^3	R^2
NLP	13.89×10^{-3}	81.73	0.9995	1.052×10^{-3}	1.051	0.9993
NSP	55.56×10^{-3}	18.99	0.9957	1.051×10^{-3}	1.049	0.9992
JSP	7.35×10^{-3}	137.93	0.9924	0.906×10^{-3}	1.059	0.9928

The observed K_L values reveal the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on adsorbent surface with constant energy. The observed b values shows that the adsorbent prefers to bind acidic ions and that speciation predominates on sorbent characteristics, when ion exchange is the predominant mechanism takes place in the adsorption of Cd(II) ion.

The Langmuir adsorption isotherm can be expressed in terms of dimensionless constant, called separation factor or equilibrium parameter (R_L). This is an essential feature of Langmuir adsorption isotherm and it can be defined in Eq. (5), where, C_o is the initial concentration of the Cd(II) ion. The significant of equation (5) is that, when $R_L > 1$, the adsorption is unfavorable; when $0 < R_L < 1$, the adsorption is favorable and when $R_L = 0$, the adsorption is irreversible. Here the range of R_L values are 0.55 - 0.75, 0.84 - 0.93 and 0.42 - 0.65 for NLP, NSP and JSP, respectively. According to Ganjidoust et al**.** [117], the adsorption is favorable since the obtained value of $\mathrm{R_L}$ is in the range of zero to one.

The adsorption of Cd(II) ion on NLP, NSP and JSP were also employed the Freundlich equation (Eq. 2) and the constants K_f and $1/n$ are incorporating all factors affecting the adsorption capacity and intensity of adsorption, respectively. Linear plots of log C_e vs log C_{ads} showed that the adsorption of Cd(II) ion follows the Freundlich isotherm model in Figures 29, 30 and 31.

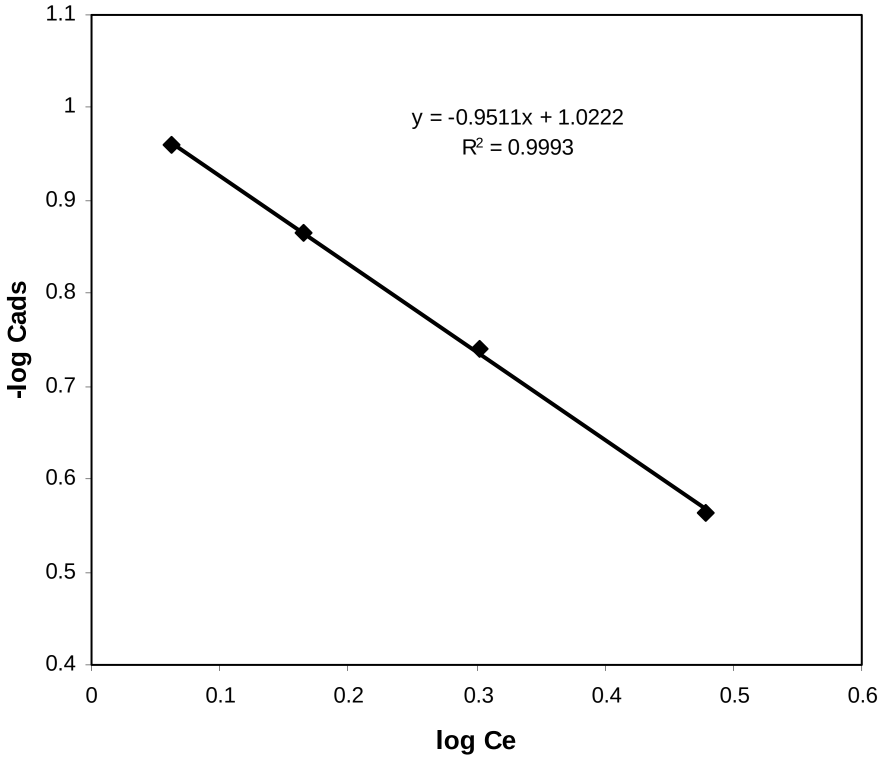

Figure 29: Freundlich isotherm model for adsorption of Cd(II) on NLP

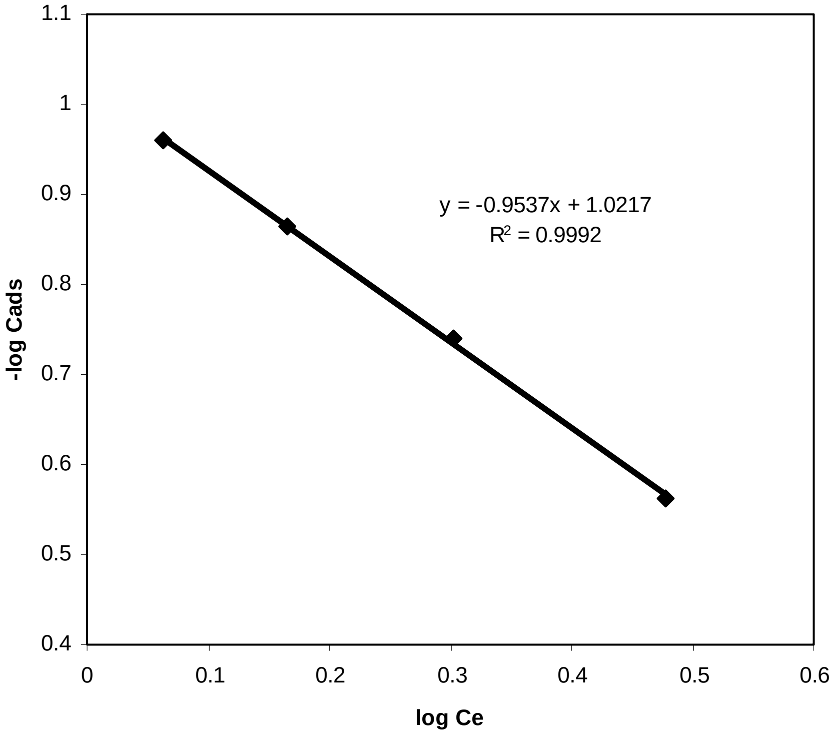

Figure 30: Freundlich isotherm model for adsorption of Cd(II) on NSP

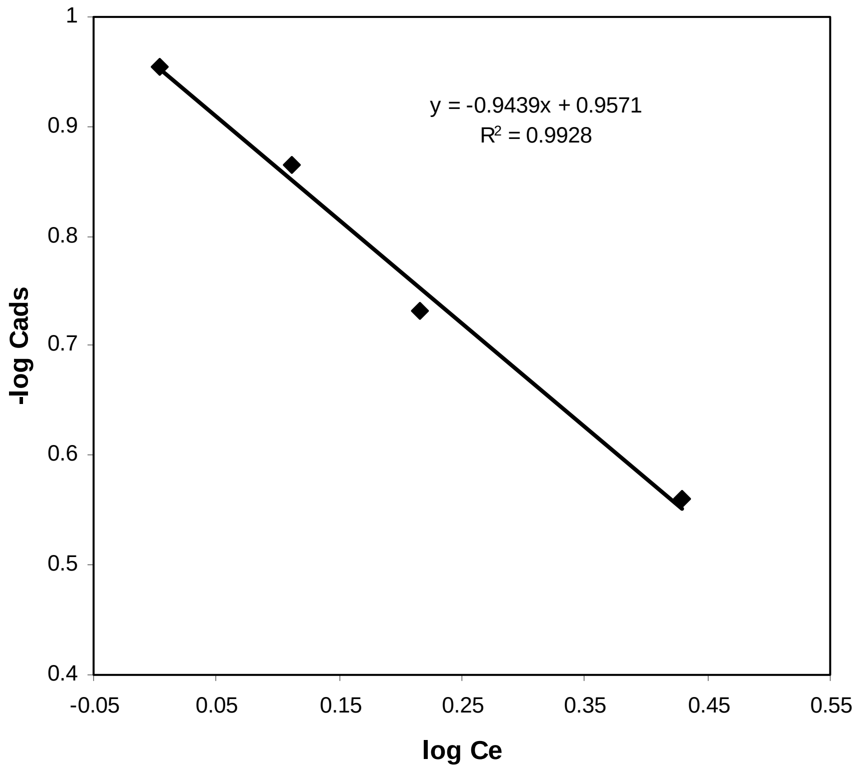

Figure 31: Freundlich isotherm model for adsorption of Cd(II) on JSP

If 1/*n* <1, bond energies increase with surface density, if 1/*n*>1, bond energies decrease with surface density and if 1/*n* =1 all surface sites are equivalent [118]. By plotting log C_{ads} vs log C_e, straight line were obtained as shown for NLP, NSP and JSP in Figures 29, 30 and 31, respectively. The adsorption also followed the Freundlich isotherm, i.e. the adsorptions were favorable. The values of K_L, *b*, K_f, and *n* for the NLP, NSP and JSP were listed in Table 9.

The values of K_f and *n* given in the Table 10 showed that the increase in negative charges on the adsorbent surface, that makes electrostatic force like Van der Waal's between the adsorbent surface and Cd(II) ion. This increases the adsorption of Cd(II) ion. The higher atomic weight, large size and radius of the Cd(II) ion have limits the possibility of the adsorption of cadmium ion onto adsorbent in higher concentration. However, the values clearly show the dominance in adsorption capacity. The values of n are greater than one indicating the adsorption is much more favorable.

The equilibrium constants of adsorption of Cd(II) onto adsorbent is related to the free energy of adsorption [119] as shown in (Eq. 6). Values of ΔG^{o}_{ads} were recorded in Table 10. The results indicated that the values of free energy are negative, suggesting that adsorption of Cd(II) onto NLP, NSP and JSP are thermodynamically favorable.

Table 10: Free energy of adsorption data of Neem leaf Powder for Cd(II)

Initial Conc. C_o (mg/L)	Equilibrium Conc. C_e (mg/L)	Amount Adsorbed C_{ads} (mg/g)	ΔG°_{ads} (kJ/mol)
4.0	0.3328	3.6672	–5.947
6.0	0.4977	5.5023	–5.956
8.0	0.6845	7.3155	–5.867
10.0	0.8651	9.1349	–5.841

4.1.2.4 Effect of pH

The experiments carried out at different pH values showed that the adsorption percentage increases with an increase in the pH of the medium up to 6 and then decreases as depicted in the Figure 32. It is interesting to note here that the percentage of Cd(II) adsorption onto NLP increase with an increase in the pH of the medium and then decrease with further increase in pH. This indicates that no additional reagent is required to control the pH of the medium for maximum adsorption of Cd(II) onto NLP.

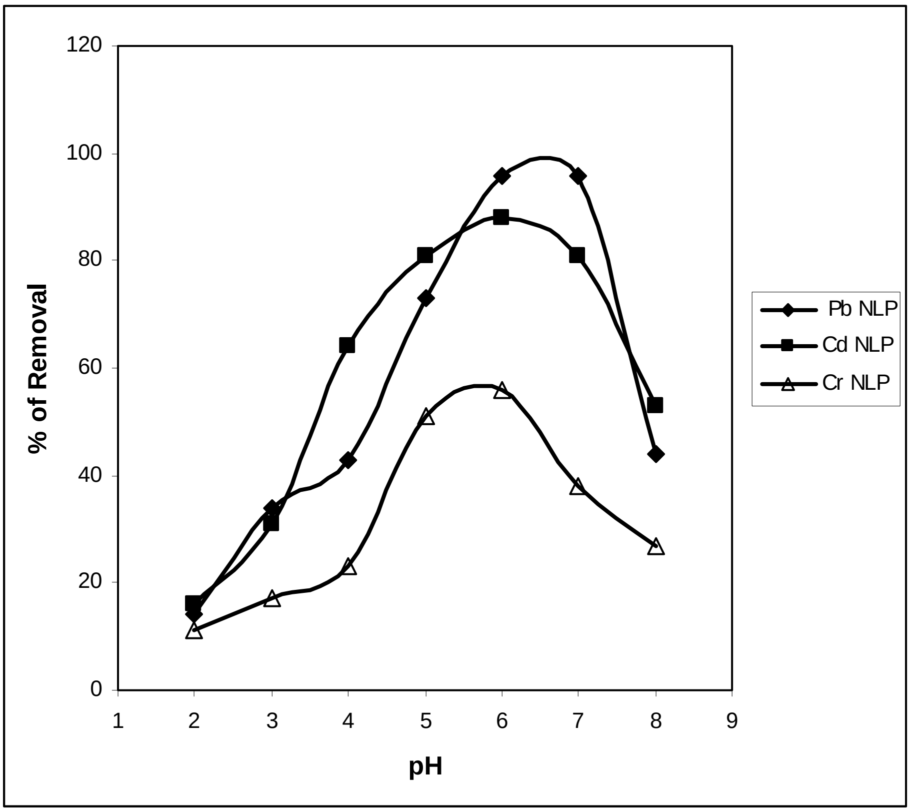

Figure 32: Effect of pH for removal of Cd (II) onto Neem Leaf Powder, contact time 300 minutes, cadmium ion 6.0 mg/L and adsorbent 1 g.

4.1.2.5 Desorption Studies

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the Cd(II) ions. If the adsorbed Cd(II) ions can be desorbed using neutral deionized water, then the attachment of the Cd(II) ions of the adsorbent is by weak bonds. If sulphuric acid or alkaline water desorp the Cd(II) ion then the adsorption is by ion exchange. The effect of various reagents used for desorption studies indicate that hydrochloric acid is a better reagent for desorption, because we could get more than 75% removal of adsorbed Cd(II). The reversibility of adsorbed Cd(II) ions in mineral acid or base is in agreement with the pH dependent adsorption as shown in Figure 32. The desorption of Cd(II) ions by mineral acids and alkaline medium indicates that the Cd(II) ions were adsorbed onto the NLP through by physisorption mechanisms. Percentage of desorption with deionized water and 0.1M HCl are listed in **Table 11.**

Table 11: Adsorption and Desorption data of Neem leaf Powder for Cd(II)

Initial Conc. C_o (mg/L)	Amount Adsorbed, C_{ads} (mg/g)	% Desorption with deionized water	% Desorption with 0.1M HCl
4	3.6676	0.151	2.756
6	5.5026	0.164	3.012
8	7.3160	0.201	3.079
10	9.1350	0.147	3.144

4.1.2.6. Adsorption Kinetics

The study of adsorption kinetics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface. The kinetics of Cd(II) ions adsorption onto NLP, NSP and JSP were analyzed using pseudo first-order and pseudo second-order kinetic models. The conformity between experimental data and the model predicted values is expressed by the correlation coefficients (R^2, values close or equal to 1). A relatively high R^2 value indicates that the model successfully describes the kinetics of metal ions adsorption.

The Pseudo First-order Equation

Applying the pseudo first-order equation, (Eq.3) (called Lagergren equation) for NLP, NSP and JSP, we obtain the Figures 33, 34 and 35.

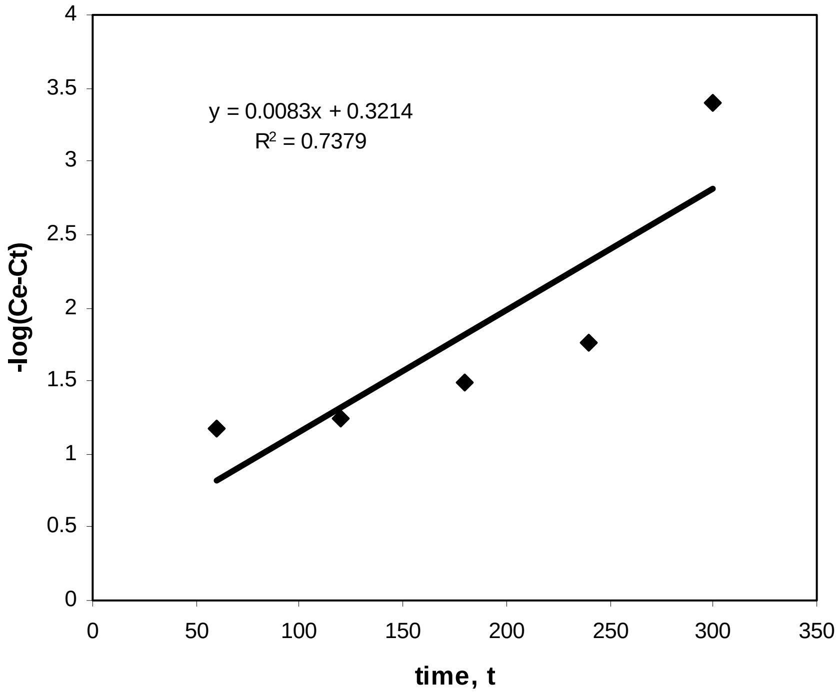

Figure 33: –log ($C_e - C_t$) vs t for removal of Cd(II) onto NLP, Equilibrium time 360 minutes, Cd(II) ion Conc. 4.0 mg/L and adsorbent 1.0 g.

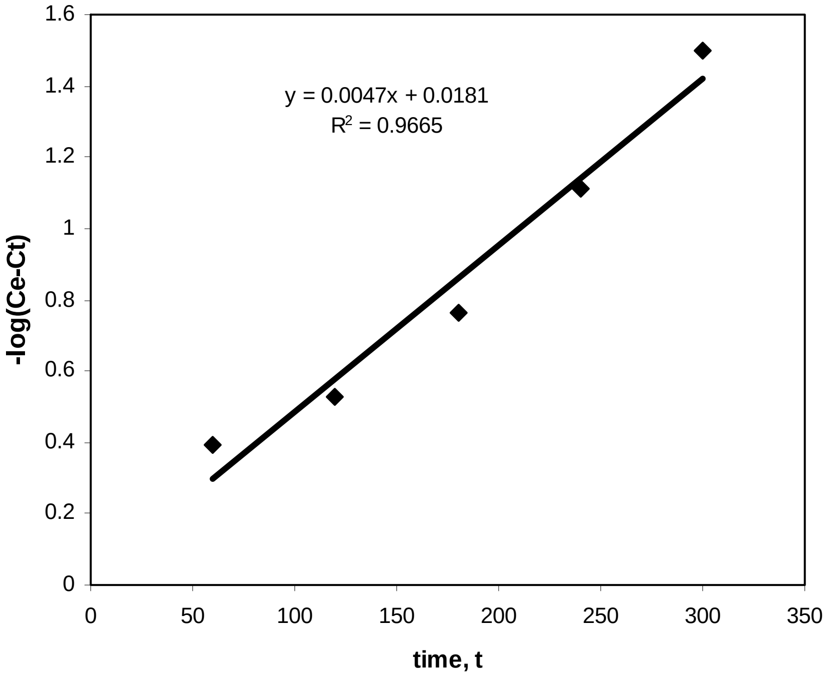

Figure 34: –log ($C_e - C_t$) vs t for removal of Cd(II) onto NSP, Equilibrium time 360 minutes, Cd(II) ion Conc. 4.0 mg/L and adsorbent 1.0 g.

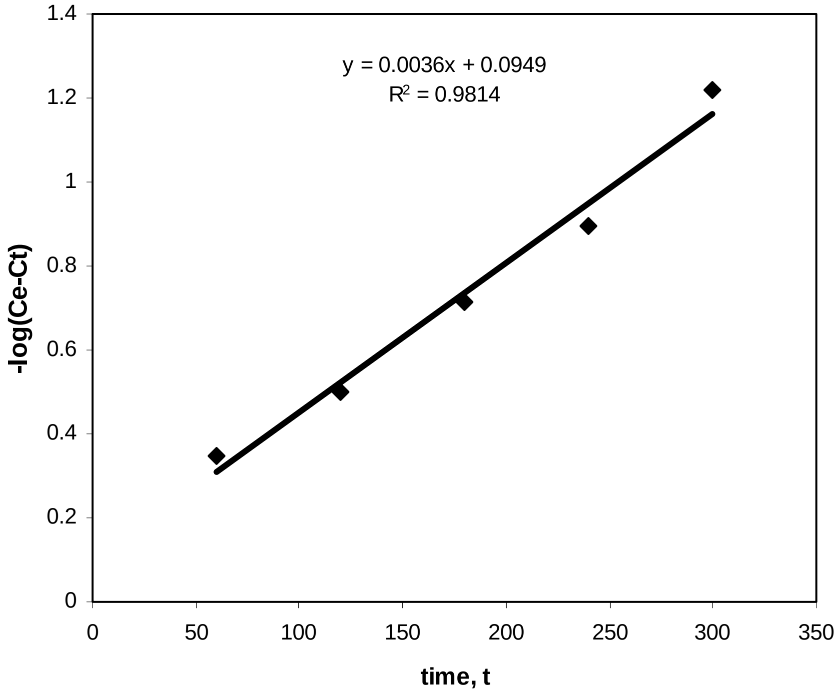

Figure 35: –log ($C_e - C_t$) vs *t* for removal of Cd(II) onto JSP, Equilibrium time 360 minutes, Cd(II) ion Conc. 4.0 mg/L and adsorbent 1.0 g.

The value of log ($C_e - C_t$) is linearly correlated with *t.* The plot of log ($C_e - C_t$) vs. *t* should give a linear relationship from which k_1 and C_e were determined from the slope and intercept of the plot, respectively and the values are shown in Table 12.

The Pseudo Second-order Equation

From the pseudo second-order adsorption kinetic rate equation (Eq.4), we were plotted (t/C_t) vs *t* for Cd(II) ions onto different adsorbent (Figures 36, 37 and 38 for NLP, NSP and JSP) and the plot show a linear relationship. The constant C_e and k_2 can be determined from the slope and intercept of the plot, respectively and listed in Table 12.

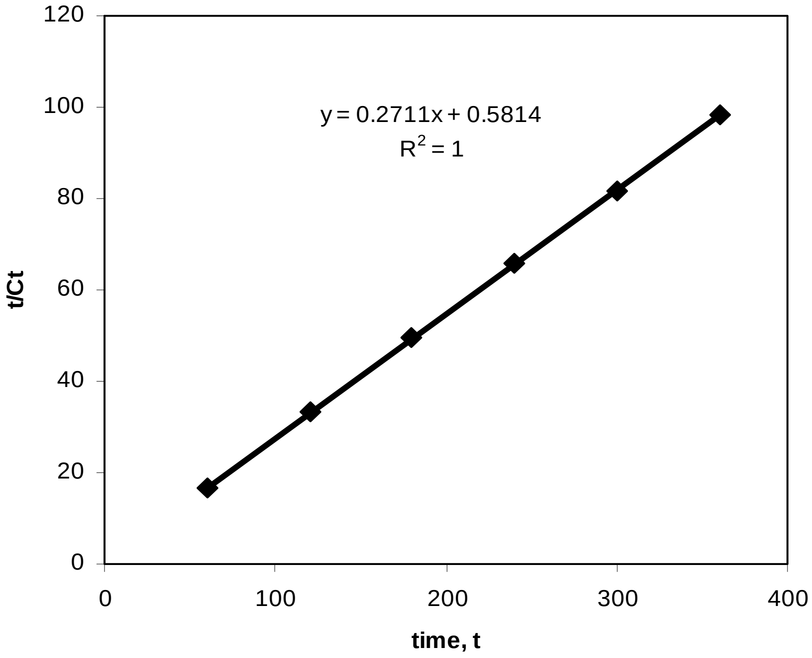

Figure 36: (t/C_t) vs t for removal of Cd(II) onto NLP, Equilibrium time 360 minutes, Cd(II) ion Conc. 4.0 mg/L and adsorbent 1.0 g.

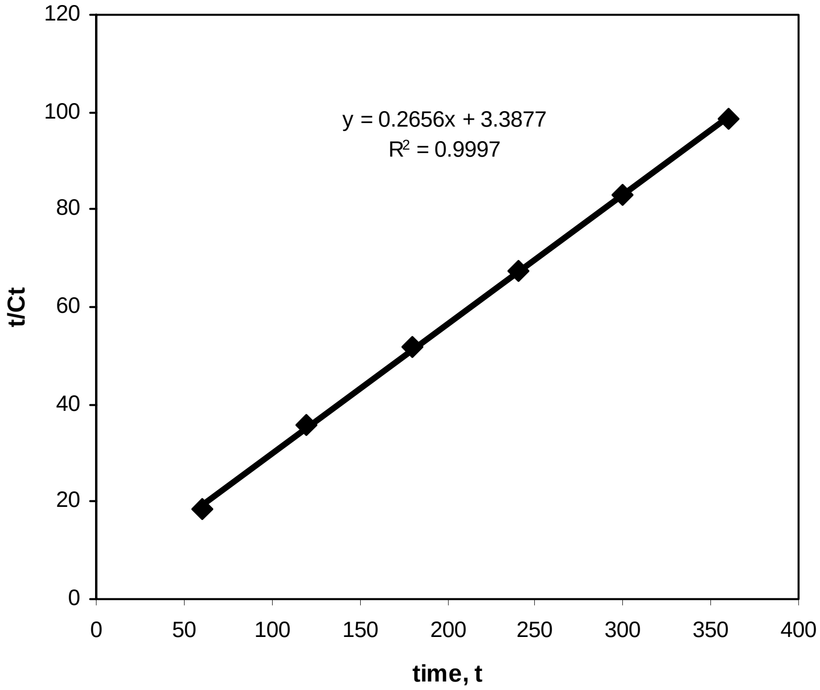

Figure 37: (t/C_t) vs t for removal of Cd(II) onto NSP, Equilibrium time 360 minutes, Cd(II) ion Conc. 4.0 mg/L and adsorbent 1.0 g.

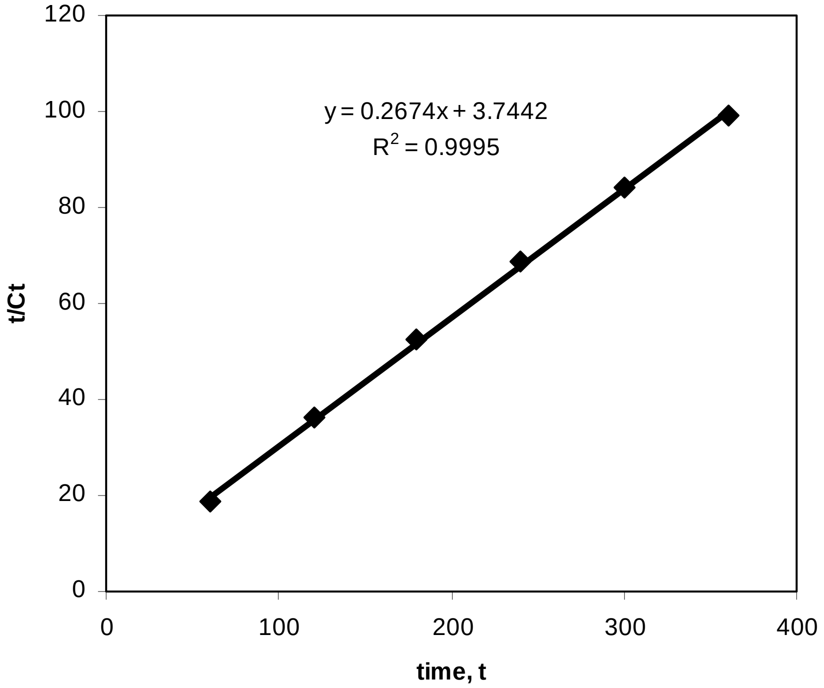

Figure 38: (t/C_t) vs t for removal of Cd(II) onto JSP, Equilibrium time 360 minutes, Cd(II) ion Conc. 4.0 mg/L and adsorbent 1.0 g.

Table 12: Adsorption kinetic constants for adsorption of Cd(II) on NLP, NSP and JSP

Adsorbent	Pseudo first order		Pseudo second order		
	k_1	R^2	k_2 (g.mg^{-1}min^{-1})	h (mg.g^{-1}.min^{-1})	R^2
NLP	0.0192	0.7379	1.264	0.1719	1
NSP	0.0108	0.9665	0.208	0.0295	0.997
JSP	0.0083	0.9814	0.191	0.0267	0.9995

4. 1. 3 Chromium

4.1.3.1 Effect of Contact Time and Initial Metal ion Concentration

The experimental results of adsorptions at various Cr(III) ion concentrations 4.0, 6.0, 8.0 and 10.0 mg/L with contact time are shown in Figures 39, 40 and 41. The equilibrium data reveal that, percent adsorption decreased with increase in initial Cr(III) ion concentration, but the actual amount of Cr(III) ion adsorbed per unit mass of JSP, NSP and NLP increased with increase in Cr(III) ion concentration. It means that the adsorption is highly dependent on initial concentration of Cr(III) ion. It is because of that at lower concentration, the ratio of the initial number of cadmium ion to the available surface area is low subsequently the fractional adsorption becomes independent of initial concentration. However, at high concentration the available sites of adsorption becomes fewer and hence the percentage removal of Cr(III) ion is dependent upon initial concentration [113]. Equilibrium have established at 5 hours for all concentrations. Figures 39, 40 and 41 reveal that the curves are single, smooth, and continuous, leading to saturation, suggesting the possible monolayer coverage of the Cr(III) ion on the JSP, NSP and NLP surface

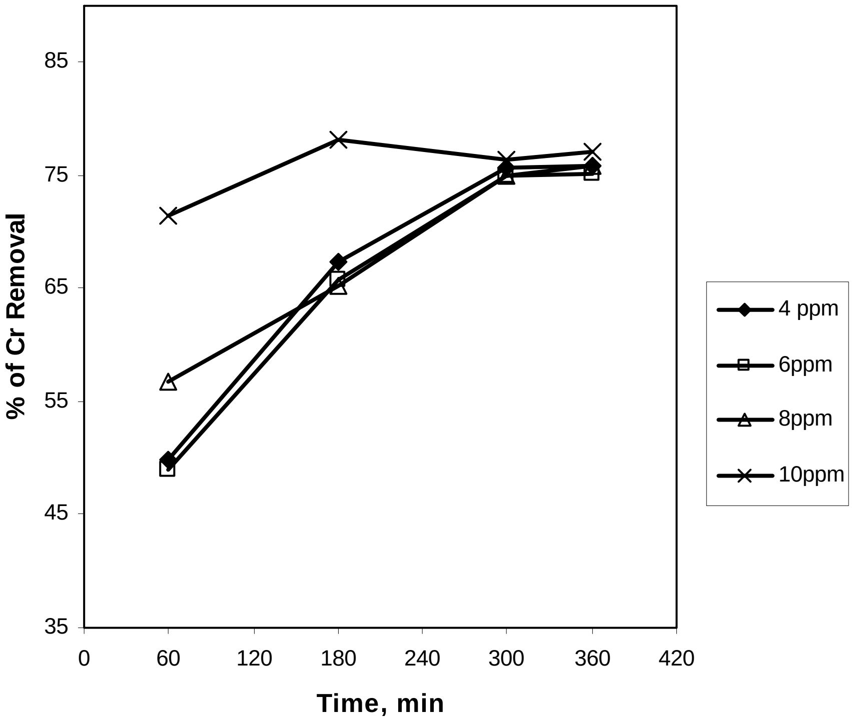

Figure 39: % of Cr(III) Removal vs Contact time with JSP

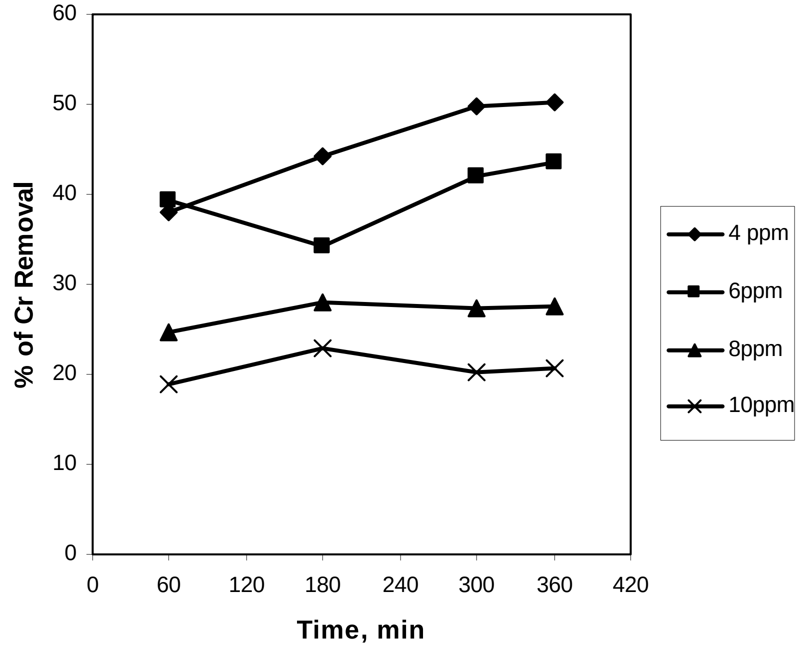

Figure 40: % of Cr(III) Removal vs Contact time with NSP

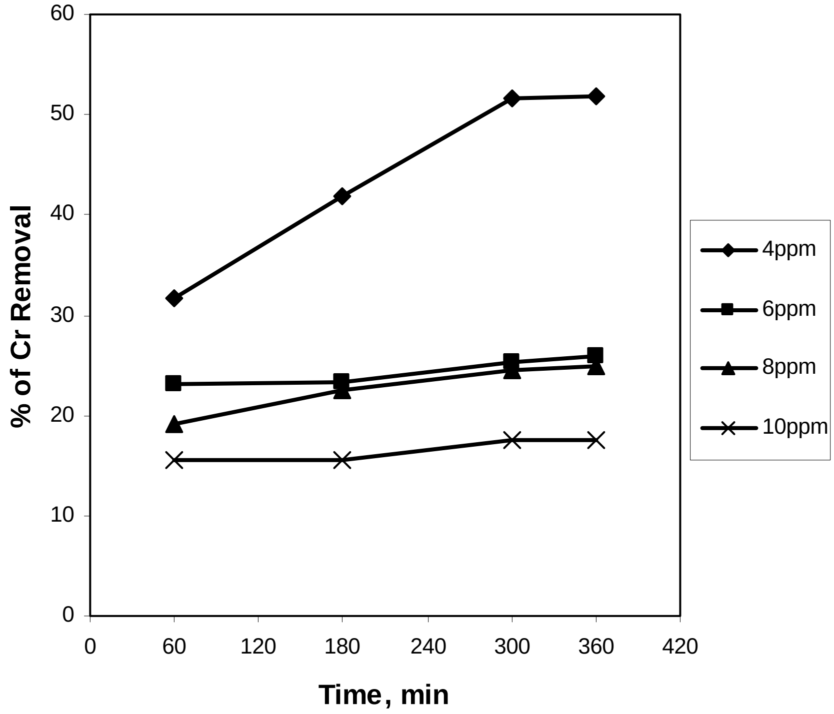

Figure 41: % of Cr(III) Removal vs Contact time with NLP

4. 1. 3. 2 Effect of Adsorbent Dosage

The effect of adsorbent dosage on the removal capacity was also studied for NSP. For NSP, the removal capacity of Cr(III)ion was determined by passing different concentrated Cr(III) solutions (4.0 mg/L- 10.0mg/L) through the column using a fixed amount (1g) of adsorbent. Secondly, the data were collected for varying amounts of the adsorbent (NSP) at a fixed concentration of (6.0 ppm) Cr(III) ion-solution. The Cr(III) ion concentration was measured in the outlet to calculate the percent of removal shown in Table 13.

Table 13: Data for the fixed amount of adsorbent dosage of NSP equilibrium at 300 minutes

Amount Adsorbed (g)	Initial Conc. C_o (ppm)	Equilb. Conc. C_e (ppm)	% of Removal
1 g	4.0	2.0103	49.74
	6.0	3.6404	39.33
	8.0	6.0295	24.63
	10.0	8.1164	18.84

The relation between the percentages of removal of Cr(III) with adsorbent dosage was shown in Figure 42. From this curve, it is clear that the percent of removal of Cr(III) increased with the increase of adsorbent dosage and reached almost saturation (53.06%), above 2 g of adsorbents for the 6.0 ppm Cr(III) in 100 ml solution.

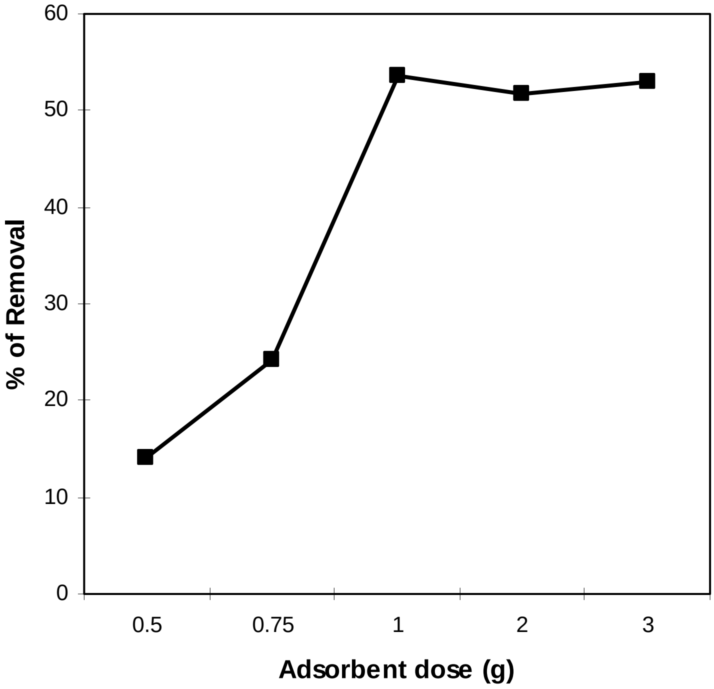

Figure 42: Effect of adsorbent dosage (NSP) on the removal of Cr(III) with fixed concentrated solution (6.0 mg/L) and contact time 300 minutes

4. 1. 3. 3 Evaluation of Bio-sorption Efficiency

The biosorption data for the removal of Cr(III) was correlated with Langmuir and Freundlich models [116]. The Langmuir equation (Eq.1), which is valid for monolayer sorption on a surface containing a limited number of sites, predicting a homogeneous distribution of sorption energies, were applied for JSP, NSP and NLP.

The linear plots of $1/C_e$ versus $1/C_{ads}$ suggest the applicability of the Langmuir isotherm is shown in Figures 43, 44 and 45 for JSP, NSP and NLP, respectively. Values of K_L and b were determined from slope and intercepts of the plots and are presented in Table 14.

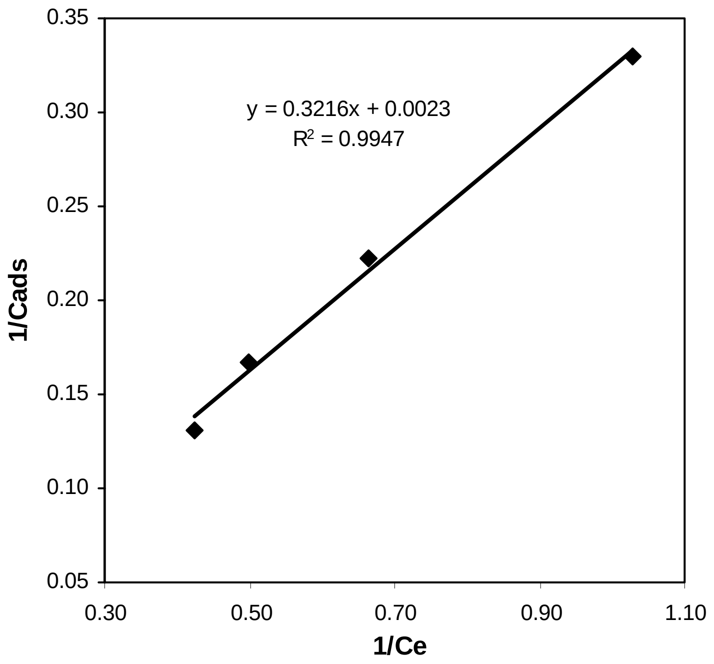

Figure 43: Langmuir isotherm model for adsorption of Cr(III) on JSP

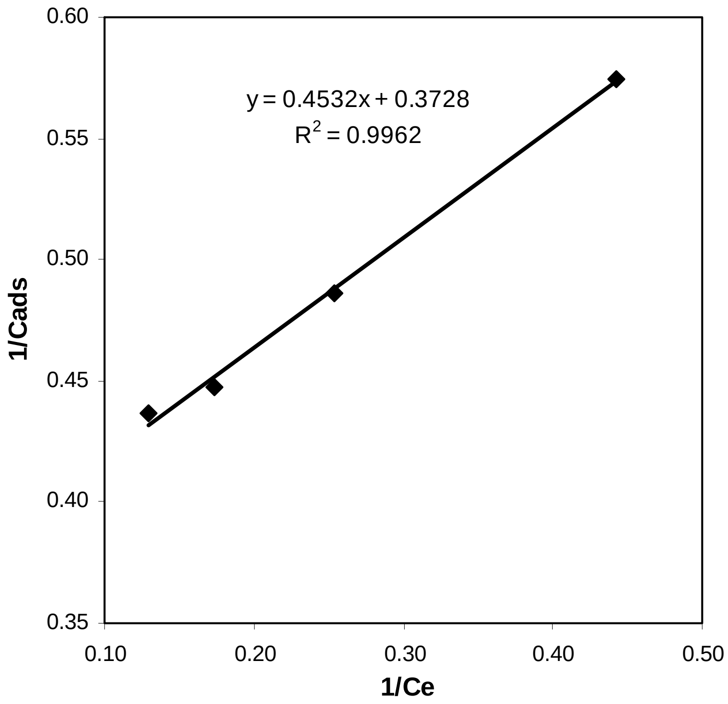

Figure 44: Langmuir isotherm model for adsorption of Cr(III) on NSP

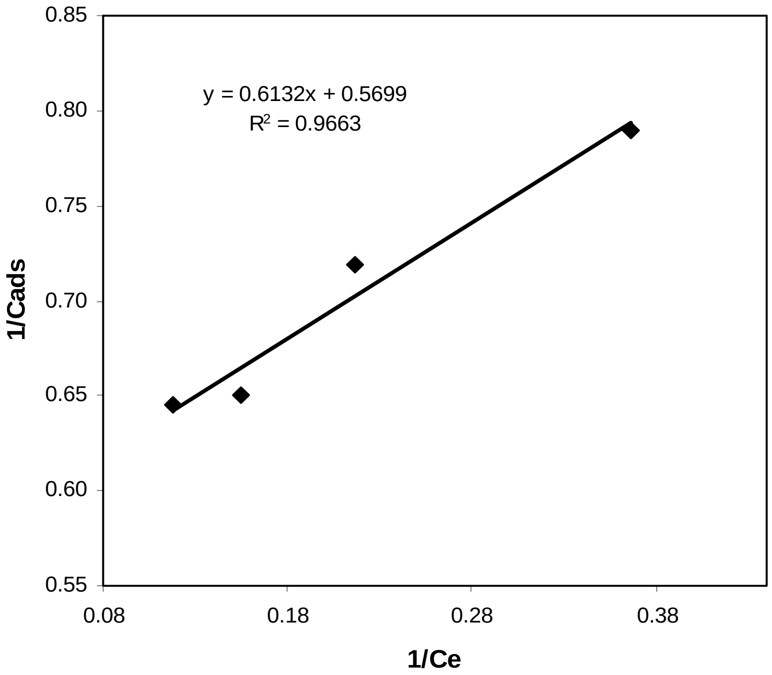

Figure 45: Langmuir isotherm model for adsorption of Cr(III) on NLP

Table 14: Langmuir and Freundlich constants derived from experimental data of adsorption of Cr(III) on JSP, NSP and NLP

Adsorbent	Langmuir Constants			Freundlich Constants		
	K_L kg/kg (Cd/Ads)	b m^3 /kg	R^2	K_f kg/kg (Cd/Ads)	n kg/m^3	R^2
JSP	43.478×10^{-3}	7.15	0.9947	0.3053×10^{-3}	0.983	0.9916
NSP	0.268×10^{-3}	822.59	0.9962	0.1395×10^{-3}	3.631	0.9960
NLP	0.176×10^{-3}	929.39	0.9663	0.1045×10^{-3}	5.197	0.9620

The observed K_L values conclude that the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on adsorbent surface with constant energy and no transmission of adsorbate in the plane of the adsorbent surface. The observed *b* values shows that the adsorbent prefers to bind acidic ions and that speciation predominates on sorbent characteristics, when ion exchange is the predominant mechanism takes place in the adsorption of Cr(III) ion.

Langmuir adsorption isotherm can be expressed in terms of dimensionless constant, called separation factor or equilibrium parameter (R_L) which can be defined by Eq. (5), where, C_o is the initial concentration of the adsorbate i.e. metal ion. The significant of equation 5 is that, when $R_L > 1$, the adsorption is unfavorable; when $0 < R_L < 1$, the adsorption is favorable and when $R_L = 0$, the adsorption is irreversible. For JSP, NSP and NLP, R_L value ranges are 0.93 – 0.97, 0.11 – 0.23 and 0.097 – 0.211, respectively. According to Ganjidoust *et al.* [117], the adsorption is favorable since the obtained value of R_L is in the range of zero to one.

The Freundlich equation (Eq.2) was also employed for the adsorption of cadmium ion on the adsorbent and K_f and $1/n$ are constants incorporating all factors affecting the adsorption capacity and intensity of adsorption, respectively. Linear plots of log C_e versus log C_{ads} shows that the adsorption of Cr(III) ion follows the Freundlich isotherm (Figures 46, 47 and 48).

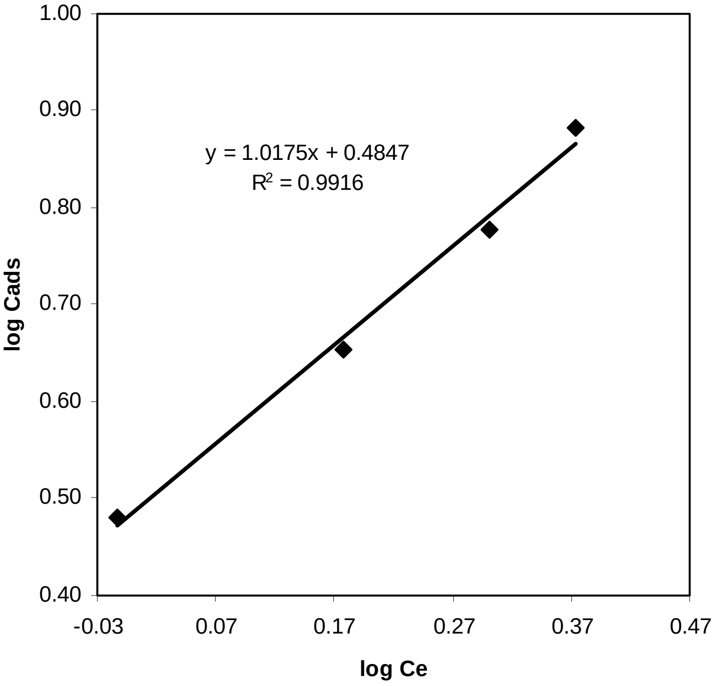

Figure 46: Freundlich isotherm model for adsorption of Cr(III) on JSP

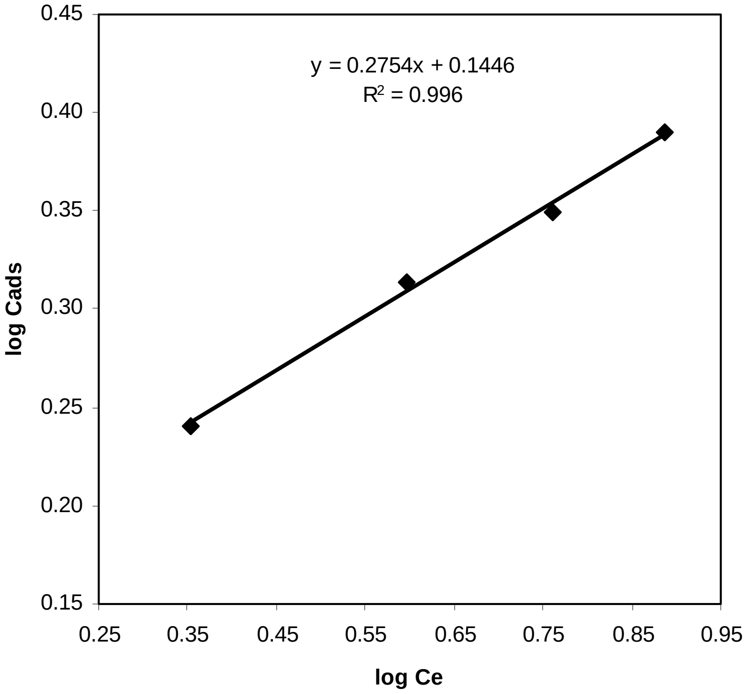

Figure 47: Freundlich isotherm model for adsorption of Cr(III) on NSP

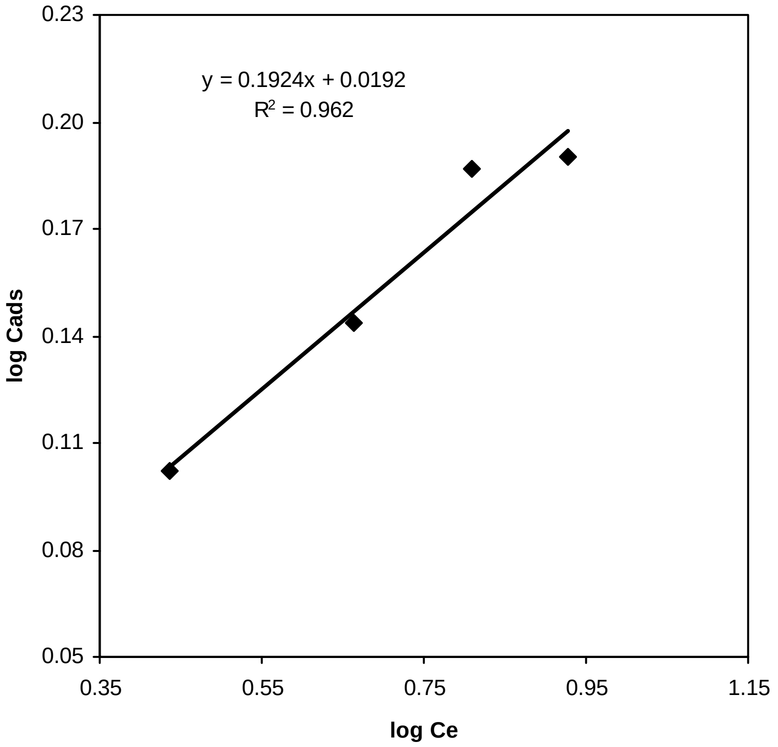

Figure 48: Freundlich isotherm model for adsorption of Cr(III) on NLP

There is a good relation between bond energy and surface density. When bond energies increase with surface density the value of 1/*n* <1, if bond energies decrease with surface density the value of 1/*n*>1, and if 1/*n* =1, all surface sites are equivalent [118]. By plotting log C_{ads} vs log C_e, a straight line was obtained as shown for JSP, NSP and NLP in Figure 46, 47 and 48, respectively. From the slope and intercept of the Figures 46, 47 and 48, the constants 1/*n* and K_f were found to be 0.0175, 0.2754, 0.1924 and 0.3053×10^{-3}, 0.1395×10^{-3} and 0.1045×10^{-3} respectively. This shows that the adsorption also follows the Freundlich isotherm, i.e. the adsorption is favorable. The values of K_L, *b* and K_f, *n* for the NLP adsorbent were listed in Table 14.

The equilibrium constant of adsorption of Cr(III) onto NSP and NLP is related to the free energy of adsorption [119] as shown in Eq. 6, where K_o is the equilibrium constant, C_{solid} is the solid phase concentration at equilibrium (mg/ L), C_{liquid} is the liquid phase concentration at equilibrium (mg/L), ΔG^o_{ads} is the free energy of adsorption, R is the gas constant, T is absolute temperature. Values of ΔG^o_{ads} are recorded in Table15. The ΔG^o_{ads} values are negative for the adsorption of Cr(III) onto JSP at all concentrations studied, suggesting the process is thermodynamically favorable under the experimental conditions. On the other hand, ΔG^o_{ads} values for the adsorption of Cr(III) onto NSP and NLP are found to positive and the magnitude of the values decrease with a decrease in concentration of the ion in solution. This result suggests that the process is not thermodynamically favorable in the studied concentration range and might be at much lower concentrations.

Table 15: Adsorption and Free Energy data for Cr(III) on NSP and NLP

Initial Conc. C_o (mg/L)	ΔG^o_{ads} (kJ/mol)		
	JSP	NSP*	NLP*
4.0	−2.8166	0.6477	1.9085
6.0	−2.7102	1.6105	2.9674
8.0	−2.7163	2.3468	3.5595
10.0	−2.9039	3.0057	4.2025

4.1. 3. 4 Effect of pH

The experiments carried out at different initial pH show that the adsorption percentage increases with increase in initial pH of the medium up to 6 and then decreases as depicted in the Figure 49. This behavior can be explained using pH of the adsorbent. In addition the decrease in adsorption of metal ions at low pH can be attributed to the competition between H^+ and metal ions. It is thus clear from Figure 49 that at lower pH, the adsorption of Cr(III) ion studied is drastically reduced. This observation was made to use of to desorb the Cr(III) ion from the adsorbed material.

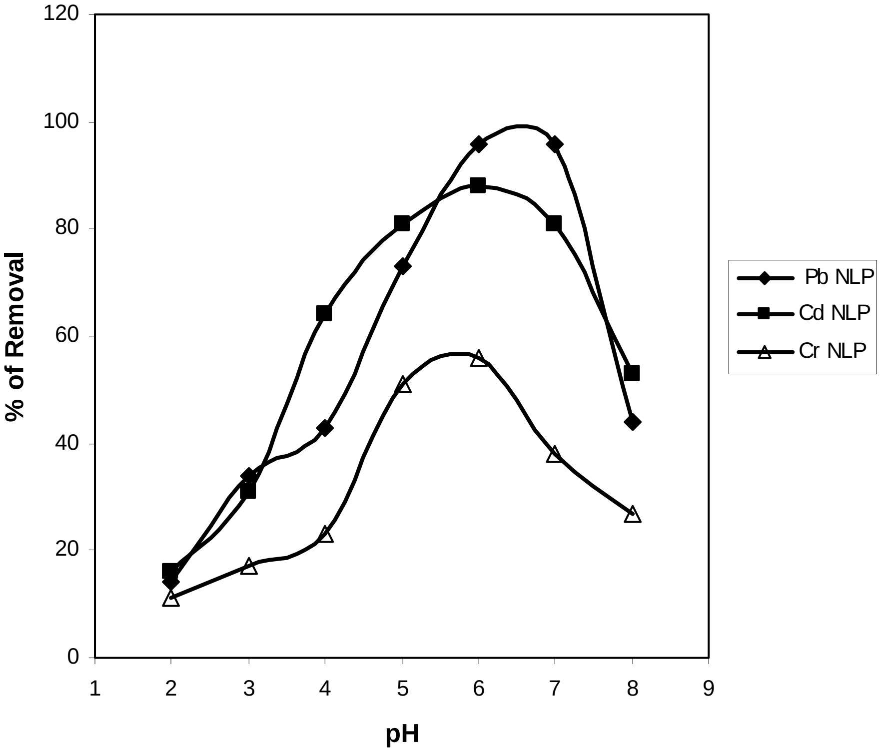

Figure 49: Effect of pH for removal of Cr(III) onto NLP, contact time 300 minutes, Cr(III) ion 6.0 mg/L and adsorbent 1 g.

4.1.3.5 Desorption Studies

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the Cr(III) ions. If the adsorbed Cr(III) ions can be desorbed using neutral pH water, then the attachment of the Cr(III) ions of the adsorbent is by weak bonds. If sulphuric acid or alkaline water desorp the Cr(III) ion then the adsorption is by ion exchange.The effect of various reagents used for desorption studies indicate that hydrochloric acid is a better reagent for desorption, because we could get more than 35% removal of adsorbed

Cr(III) using 0.1M HCl. The reversibility of adsorbed Cr(III) ions in mineral acid or base is in agreement with the pH dependent results obtained. The desorption of Cr(III) ions by mineral acids and alkaline medium indicates that the Cr(III) ions were adsorbed onto the NLP through by physisorption mechanisms. Desorption data are listed in Table 15.

Table 15: Adsorption and Desorption data for Cr(III)on Neem leaf Powder

Initial Conc. C_o (mg/L)	Amount Adsorbed, C_{ads} (mg/g)	% Desorption with deionized water	% Desorption with 0.1M HCl
4	1.2658	0.121	37.53
6	1.3916	0.134	34.10
8	1.5369	0.211	31.71
10	1.5501	0.187	35.48

4. 1. 3. 6. Adsorption Kinetics

The study of adsorption dynamics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface. The kinetics of Cr(III) ions adsorption on the different bioadsorbent of JSP, NSP and NLP were analyzed using pseudo first-order and pseudo second-order kinetic models. The conformity between experimental data and the model predicted values is expressed by the correlation coefficients (R^2, values close or equal to 1). A relatively high R^2 value indicates that the model successfully describes the kinetics of metal ions adsorption.

The Pseudo First-order Equation

Applying the pseudo first-order equation, (Eq.3) (Lagergren equation) for JSP, NSP and NLP we obtain the Figures 50, 51 and 52 respectively**.**

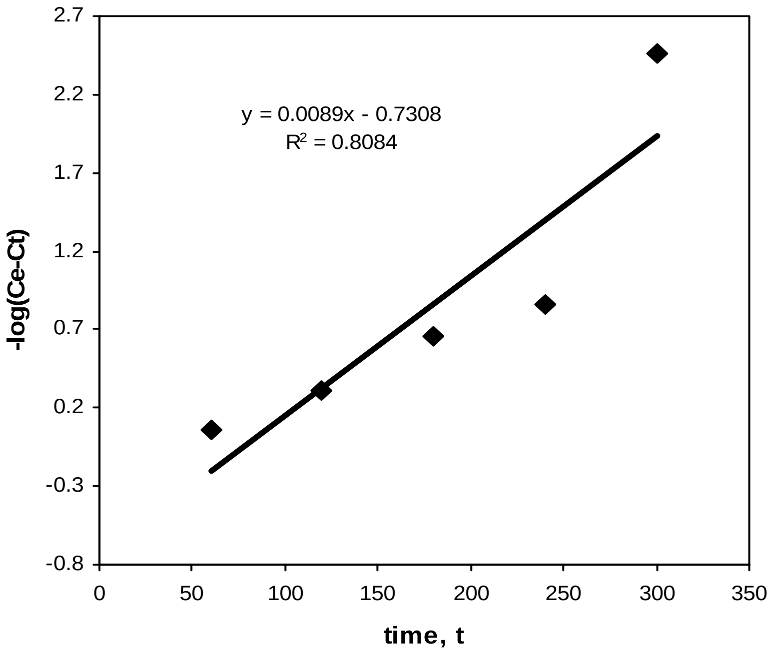

Figure 50: –log ($C_e - C_t$) vs *t* for removal of Cr(III) onto JSP, Equilibrium time 360 minutes, Cr(III) ion Conc. 4.0 mg/L and adsorbent 1.0 g.

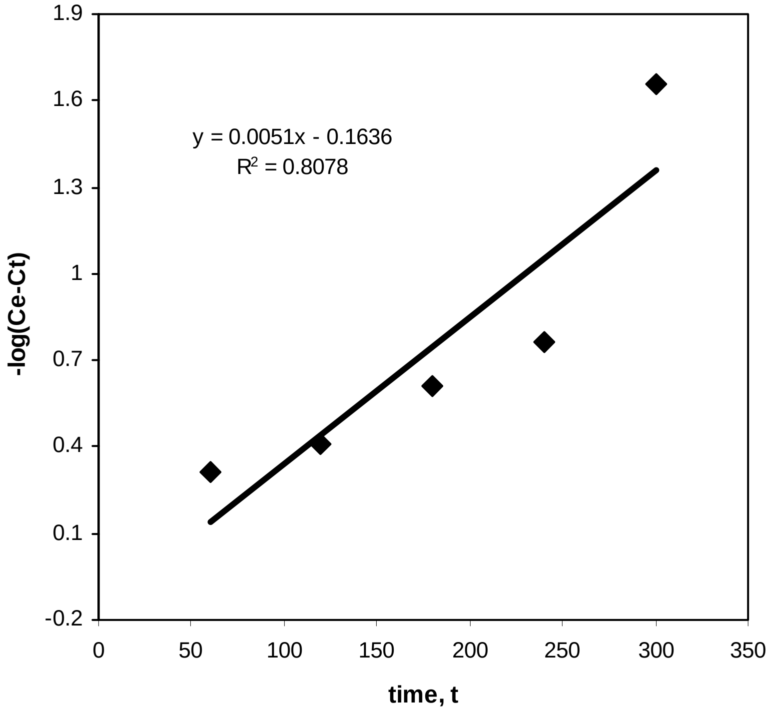

Figure 51: –log ($C_e - C_t$) vs *t* for removal of Cr(III) onto NSP, Equilibrium time 360 minutes, Cr(III) ion Conc. 4.0 mg/L and adsorbent 1.0 g.

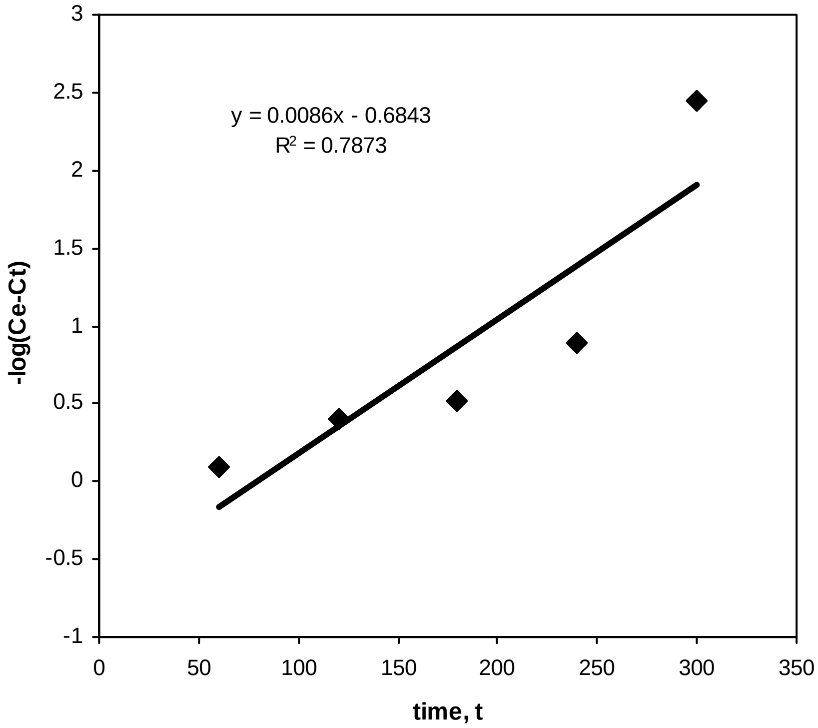

Figure 52: –log ($C_e – C_t$) vs *t* for removal of Cr(III) onto NLP, Equilibrium time 360 minutes, Cr(III) ion Conc. 4.0 mg/L and adsorbent 1.0 g.

The value of log ($C_e – C_t$) is linearly correlated with *t*. The plot of log ($C_e – C_t$) vs *t* should give a linear relationship from which k_1 and C_e were determined from the slope and intercept of the plot, respectively and the values were shown in Table 16.

The Pseudo Second-order Equation

From the pseudo second-order adsorption kinetic rate equation (Eq.4), we were plotted (t/C_t) vs *t* for Cr(III) ions onto JSP, NSP and NLP and Figures 53, 54 and 55 respectively. The plots showed a linear relationship. The constants C_e and k_2 can be determined from the slope and intercept of the plot, respectively and listed in Table 16.

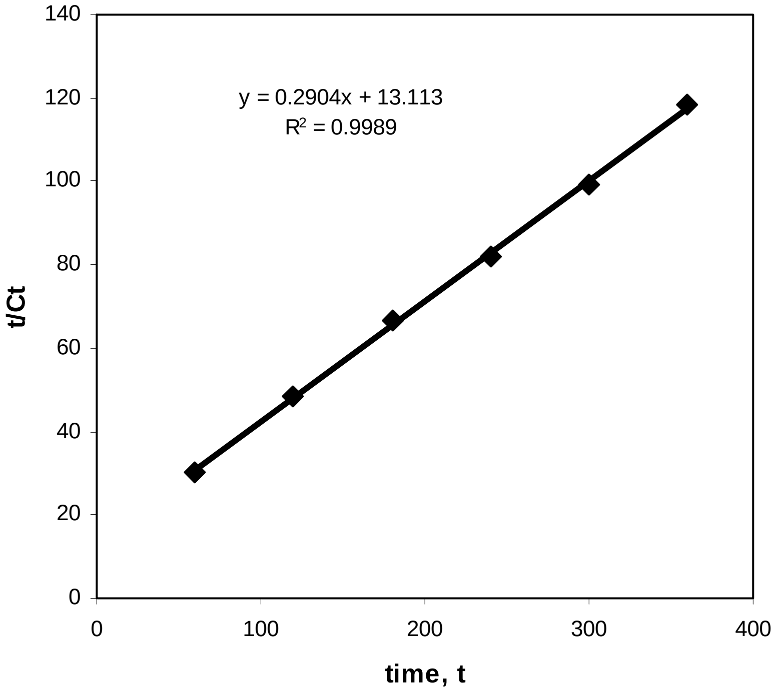

Figure 53: (t/C_t) vs *t* for removal of Cr(III) onto JSP, Equilibrium time 360 minutes, Cr(III) ion Conc. 4.0 mg/L and adsorbent 1.0 g.

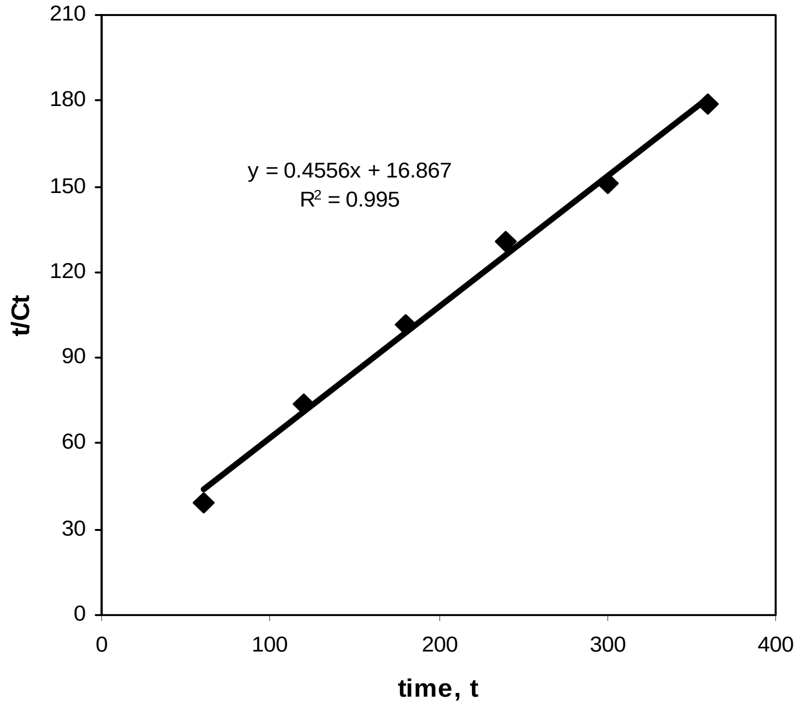

Figure 54: (t/C_t) vs *t* for removal of Cr(III) onto NSP, Equilibrium time 360 minutes, Cr(III) ion Conc. 4.0 mg/L and adsorbent 1.0 g.

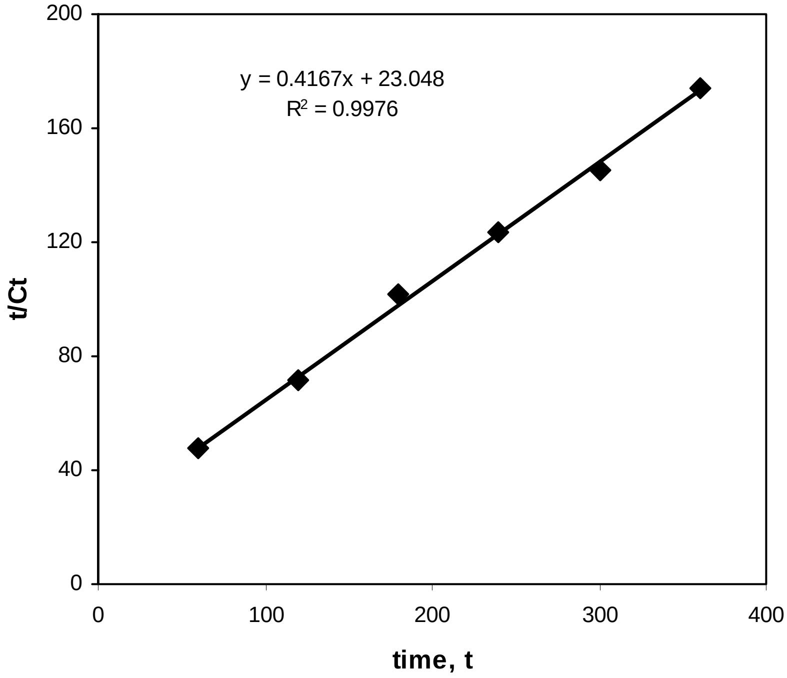

Figure 55: (t/C_t) vs t for removal of Cr(III) onto NLP, Equilibrium time 360 minutes, Cr(III) ion Conc. 4.0 mg/L and adsorbent 1.0 g.

Table 16: The adsorption kinetic model rate constants for the JSP, NSP and NLP

Adsorbent	Pseudo first order		Pseudo second order		
	k_1	R^2	k_2 (g.mg^{-1}.min^{-1})	h (mg.g^{-1}.min^{-1})	R^2
JSP	0.0205	0.8084	0.064	0.0076	0.9989
NSP	0.0118	0.8078	0.123	0.0059	0.995
NLP	0.0198	0.7873	0.075	0.0043	0.9976

4. 2 Adsorption of Metal ions from Industrial Effluents

In this experiment at first we have determined the concentration of Pb(II), Cd(II) and Cr(III) ions from the collected industrial effluent samples. We have obtained 1.02, 2.28, 3.97 mg/L Pb(II) ions, 1.14, 1.43, 2.02 mg/L Cd(II) ions and 1.17, 2.03, 9.34 mg/L Cr(III) ions from the collected samples of DEPZ, Savar; Turag River, beside the Estama field and Buriganga River, Hazaribagh , respectively. All experiments were done in room Temperature and Pressure.

4.2.1. Lead

4.2.1.1 Effect of Contact Time and Initial Metal ion Concentration

The experimental results of adsorptions at various Pb(II) ion concentrations of 1.14, 2.28 and 3.97 mg/L with contact time were shown in Figures 56, 57 and 58 of NSP, NLP and JSP, respectively. The equilibrium data reveal that, the percent adsorption increased with an increasing in initial Pb(II) ion concentration. It means that the adsorption is highly dependent on initial concentration of Pb(II) ions. It is because of that at lower concentration, the ratio of the initial number of Pb(II) ion to the available surface area is low subsequently the fractional adsorption becomes independent of initial concentration. However, at high concentration the available sites of adsorption becomes fewer and hence the percentage removal of Pb(II) ions is dependent upon initial concentration [113]. Equilibrium had established at five hours for all concentrations, but for JSP, it took six hours to attain equilibrium. Figures 56, 57 and 58 reveal that the curves are single, smooth, and continuous, leading to saturation, suggesting the possible monolayer coverage of the Pb(II) ions on the NSP, NLP and JSP surface.

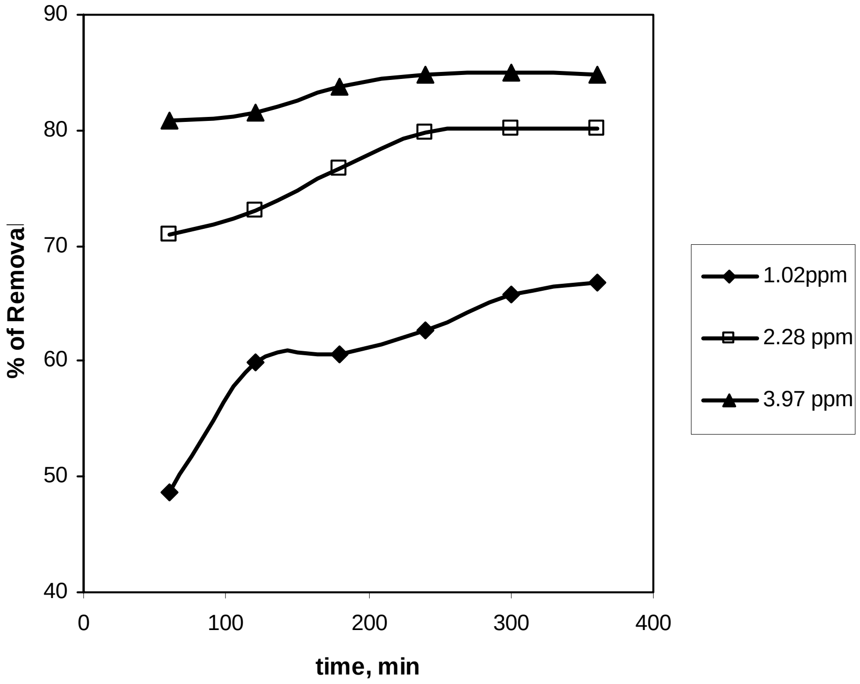

Figure 56: % of Pb Removal vs Contact time with 1.0g NSP at pH 6-7.

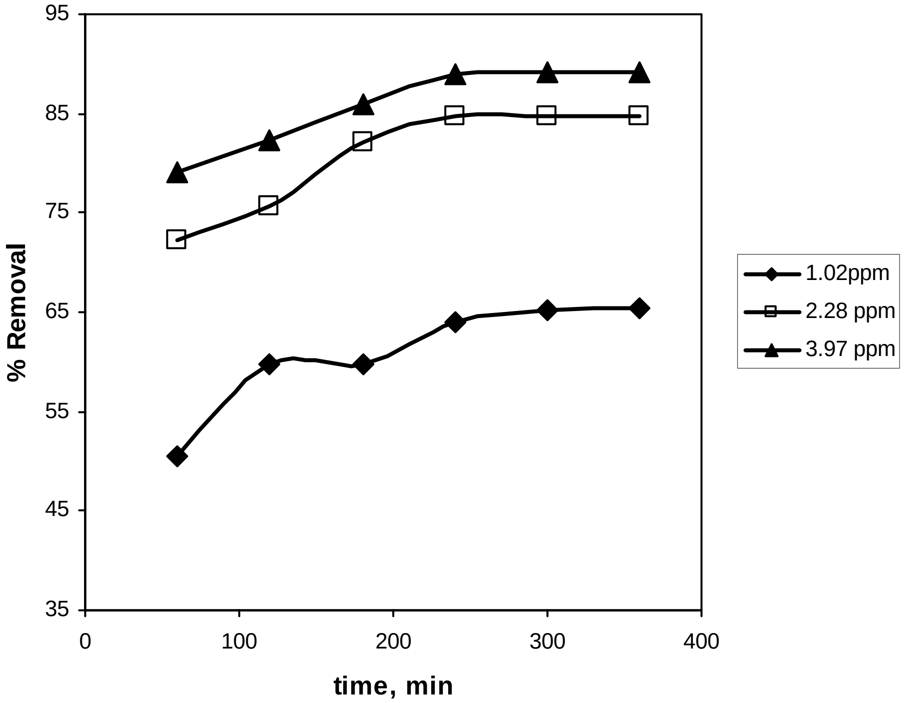

Figure 57: % of Pb Removal vs Contact time with 1.0g NLP at pH 6-7.

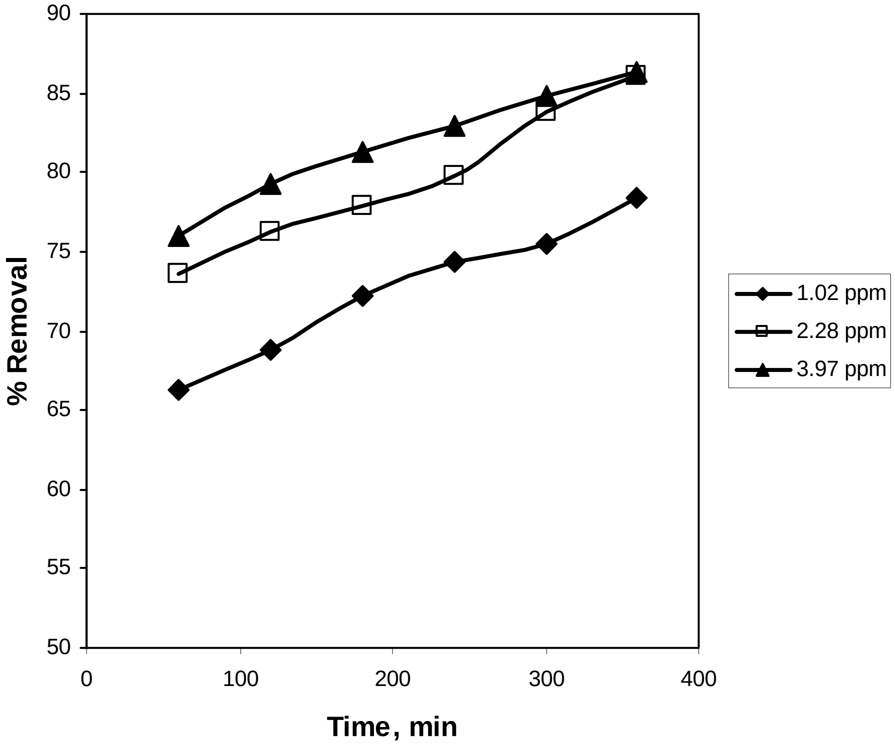

Figure 58: % of Pb Removal vs Contact time with 1.0g JSP at pH 6-7.

4.2.1.2 Evaluation of Bio-sorption Efficiency

The biosorption data for the removal of Pb(II) was correlated with Langmuir and Freundlich models [116]. The Langmuir equation (Eq.1) is valid for monolayer sorption on a surface containing a limited number of sites, predicting a homogeneous distribution of sorption energies.

Using the Langmuir equation (Eq.1), the linear plots of $1/C_{ads}$ versus $1/C_e$ suggest the applicability of the Langmuir isotherm was shown in Figures 59, 60 and 61 for NSP, NLP and JSP, respectively.

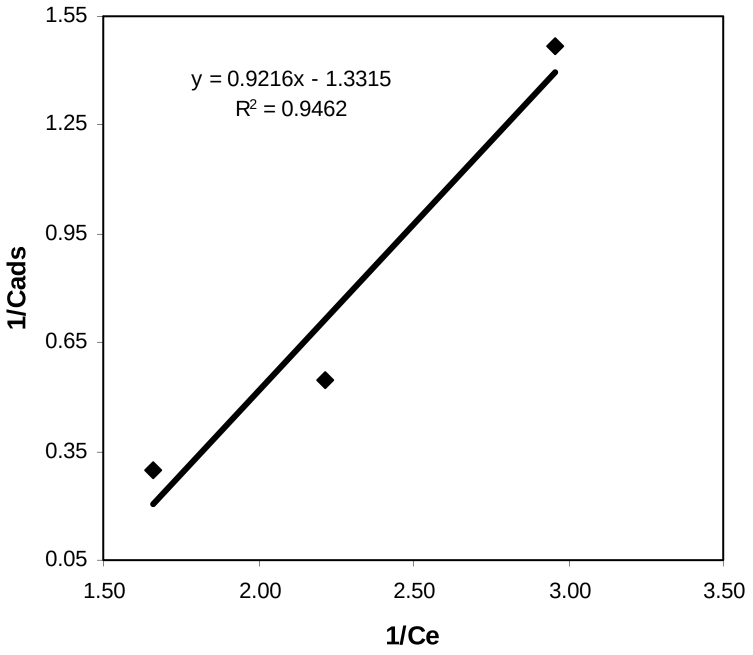

Figure 59: Langmuir isotherm model for adsorption of Pb(II) on NSP

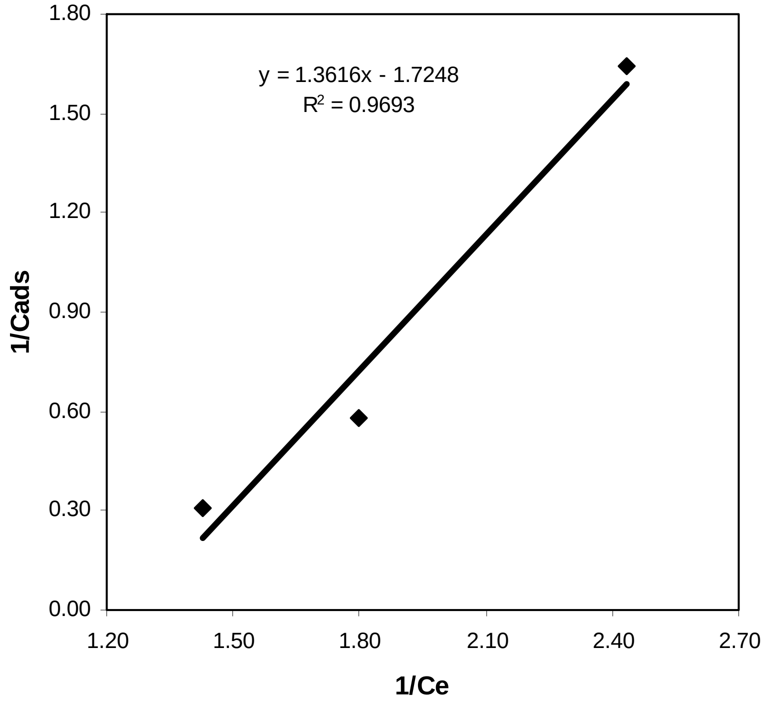

Figure 60: Langmuir isotherm model for Pb(II) adsorption onto NLP

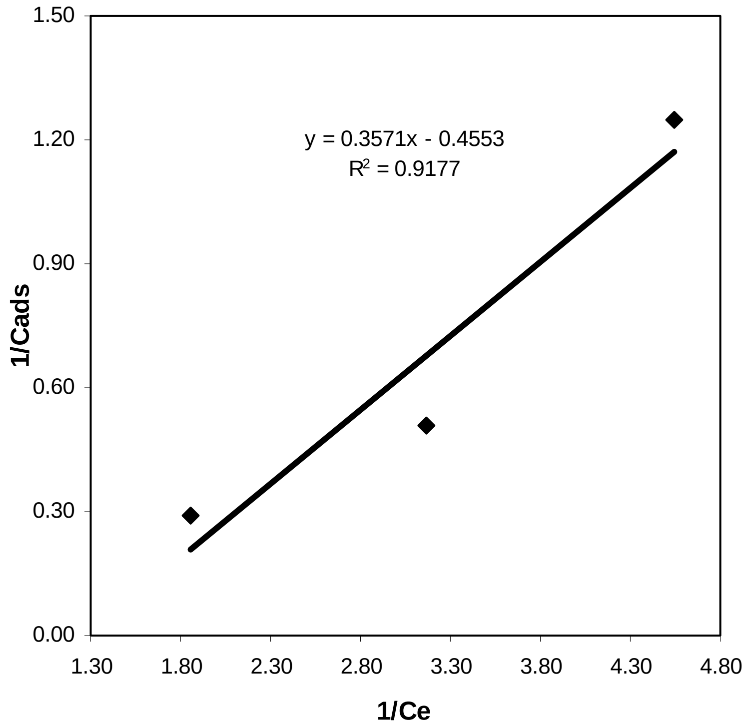

Figure 61: Langmuir isotherm model for adsorption of Pb(II) onto JSP

The Freundlich equation (Eq.2) was also employed for the adsorption of Pb(II) ions onto NSP, NLP and JSP. The constants K_f and $1/n$ incorporate all factors affecting the adsorption capacity and intensity of adsorption, respectively. Linear plots of log C_{ads} versus log C_e shows that the adsorption of Pb(II) ions with different adsorbent and correlate with Freundlich isotherm (Figures 62, 63 and 64).

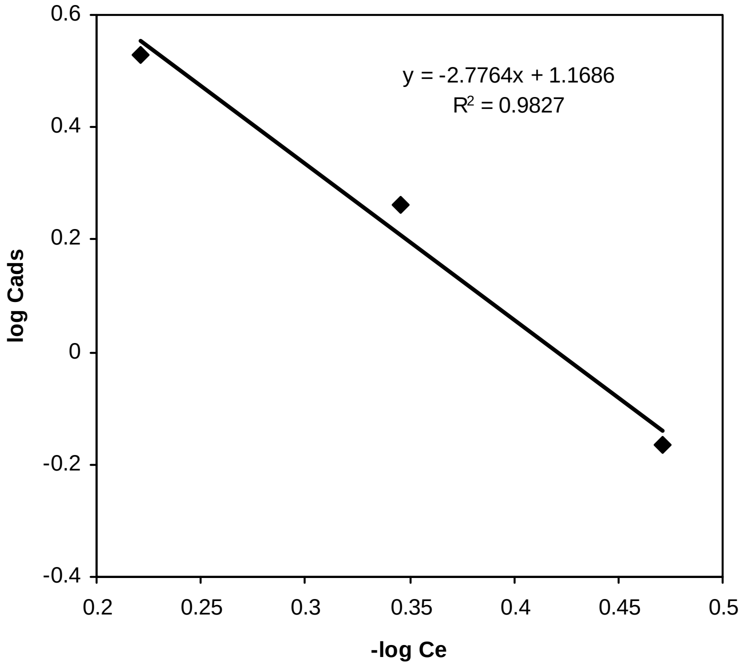

Figure 62: Freundlich isotherm model for adsorption of Pb(II) onto NSP

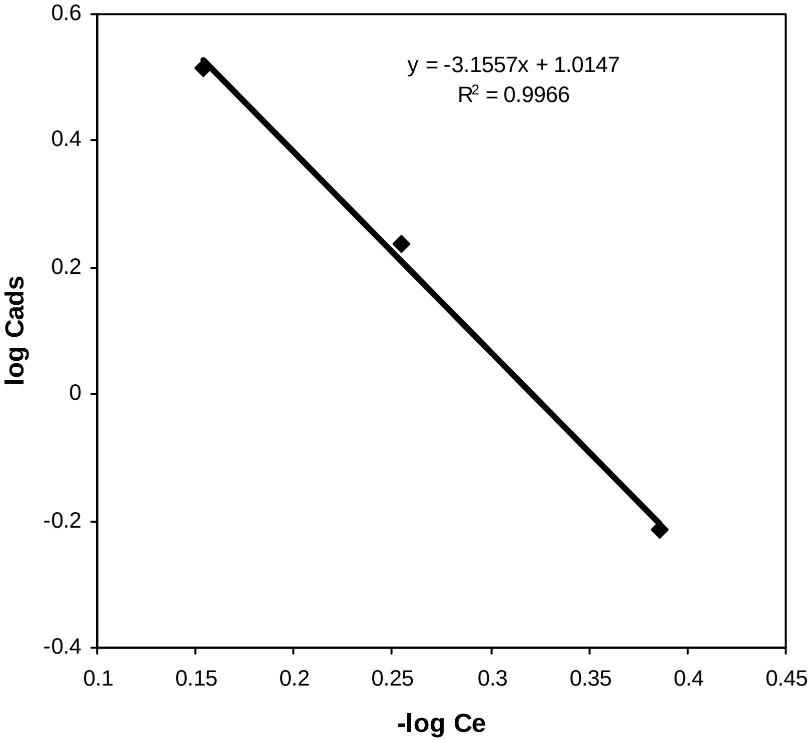

Figure 63: Freundlich isotherm model for adsorption of Pb(II) onto NLP

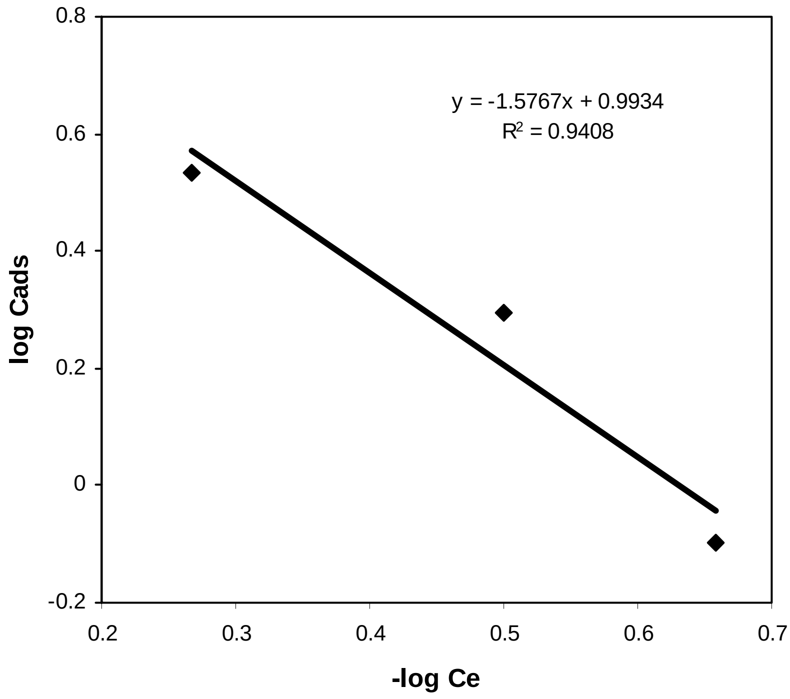

Figure 64: Freundlich isotherm model for adsorption of Pb(II) onto JSP

4. 2. 2. Cadmium

4.2.2.1 Effect of Contact Time and Initial Metal ion Concentration

The experimental results of adsorptions at various Cd(II) ion concentrations of 1.14, 1.43 and 2.02 mg/L with contact time were shown in Figures 65, 66 and 67 NSP, NLP and JSP respectively. The equilibrium data reveal that, the percent of adsorption increased with increasing in initial Cd(II) ion concentration but for JSP, lower concentration of Cd(II) ion was higher adsorption. It means that the adsorption is highly dependent on initial concentration of Cd(II) ions. Equilibrium have established at five hours for all concentrations except for JSP. Figures 65, 66 and 67 reveal that the curves are single, smooth, and continuous, leading to saturation, suggesting the possible monolayer coverage of the Cd(II) ions on the NSP, NLP and JSP surface.

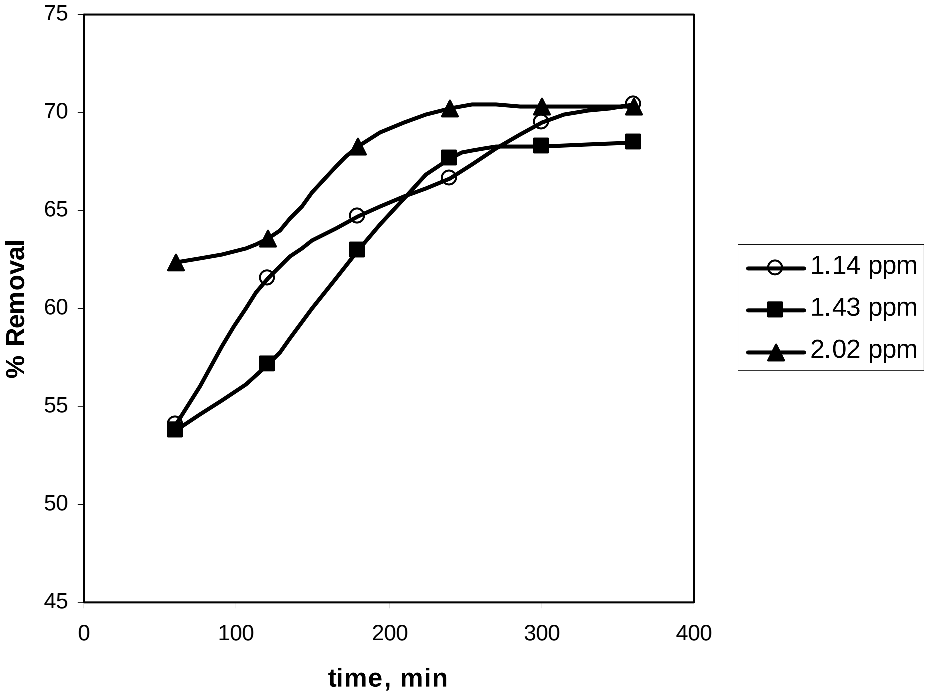

Figure 65: % of Cd(II) Removal vs Contact time with 1.0g NSP at pH 6-7.

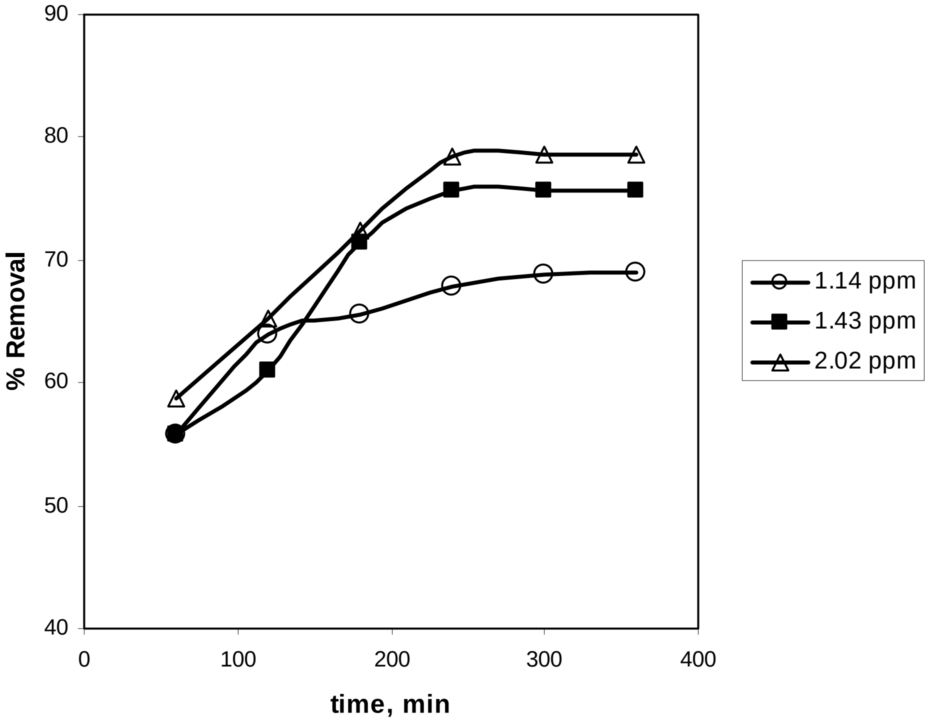

Figure 66: % of Cd(II) Removal vs Contact time with 1.0g NLP at pH 6-7.

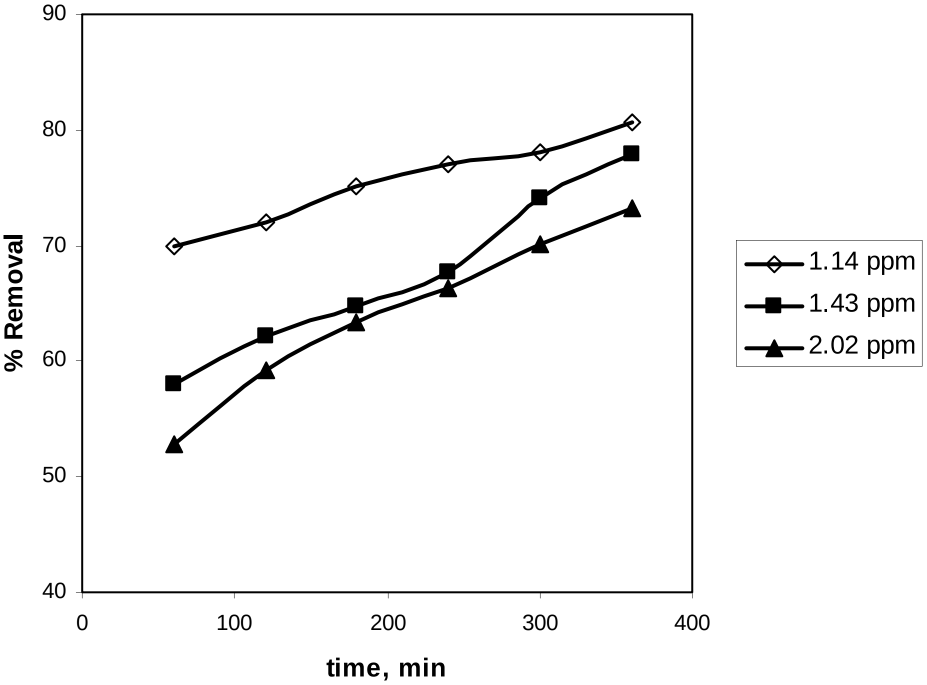

Figure 67: % of Cd(II) Removal vs Contact time with 1.0g JSP at pH 6-7.

4.2.2.2 Evaluation of Bio-sorption Efficiency

Langmuir and Freundlich isotherm models were considered for determination of biosorption efficiency. The biosorption data for the removal of Cd(II) was correlated with Langmuir and Freundlich models [116]. The Langmuir equation (Eq.1) is valid for monolayer sorption on a surface containing a limited number of sites, predicting a homogeneous distribution of sorption energies.

Using the Langmuir equation (Eq.1), the linear plots of $1/C_{ads}$ versus $1/C_e$ suggest the applicability of the Langmuir isotherm is shown in Figures 68, 69 and 70 for NSP, NLP and JSP, respectively.

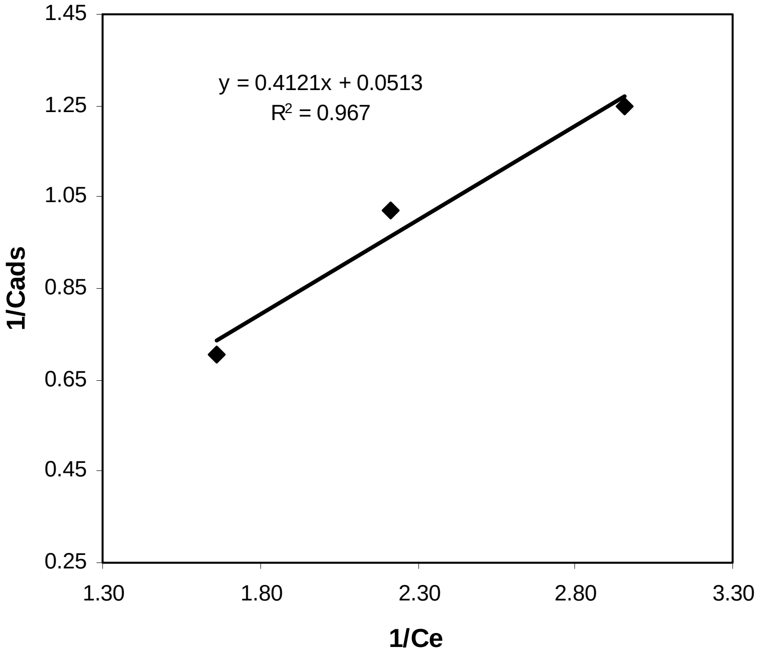

Figure 68: Langmuir isotherm model for adsorption of Cd(II) onto NSP

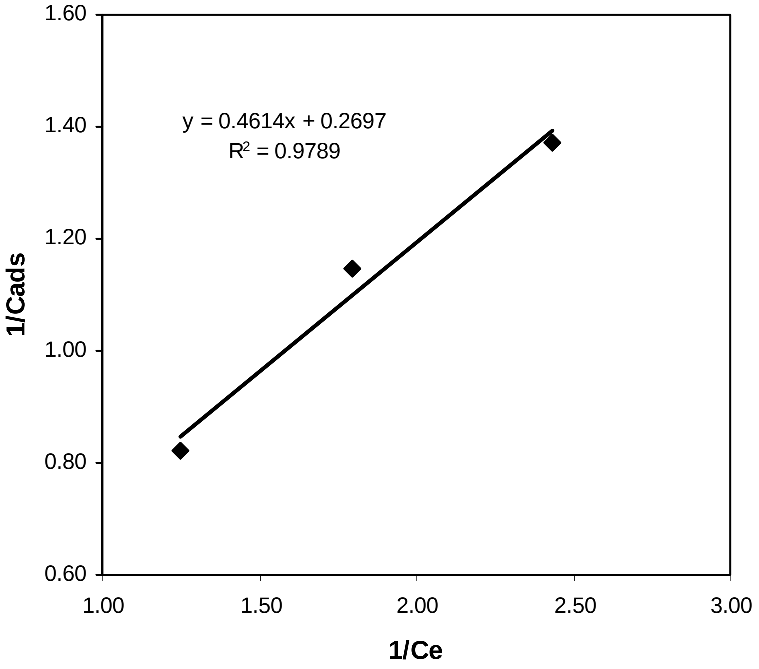

Figure 69: Langmuir isotherm model for adsorption of Cd(II) onto NLP

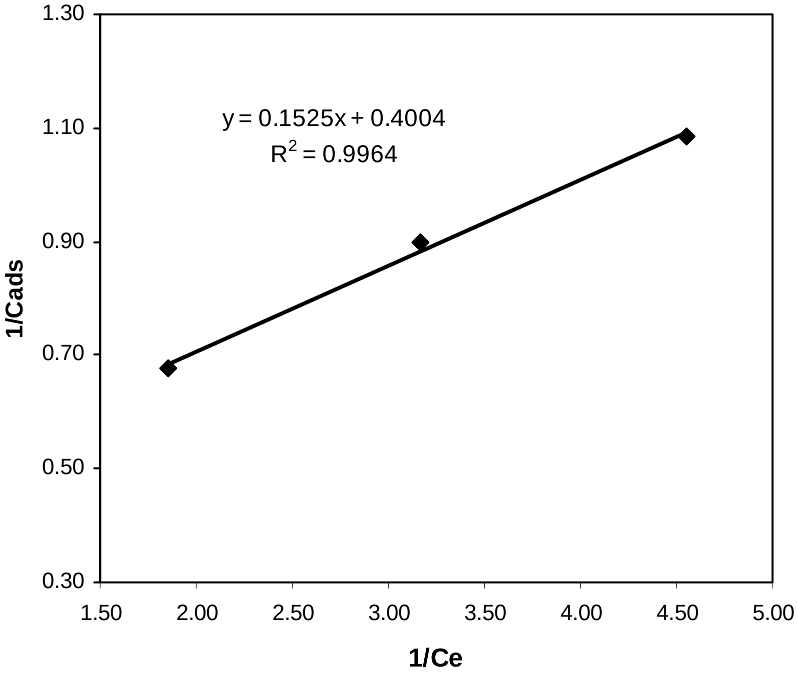

Figure 70: Langmuir isotherm model for adsorption of Cd(II) onto JSP

The adsorption data of Cd(II) ion onto NSP, NLP and JSP were also employed for Freundlich isotherm model. Linear plots of log C_{ads} versus log Ce shows that the adsorption of Cd(II) ions with different adsorbent follow the Freundlich isotherm (Figures 71, 72 and 73).

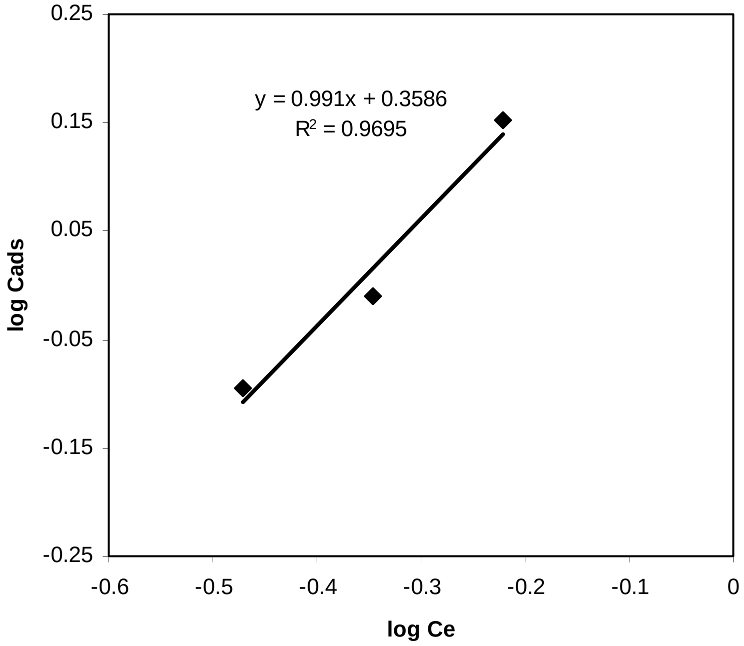

Figure 71: Freundlich isotherm model for adsorption of Cd(II) onto NSP

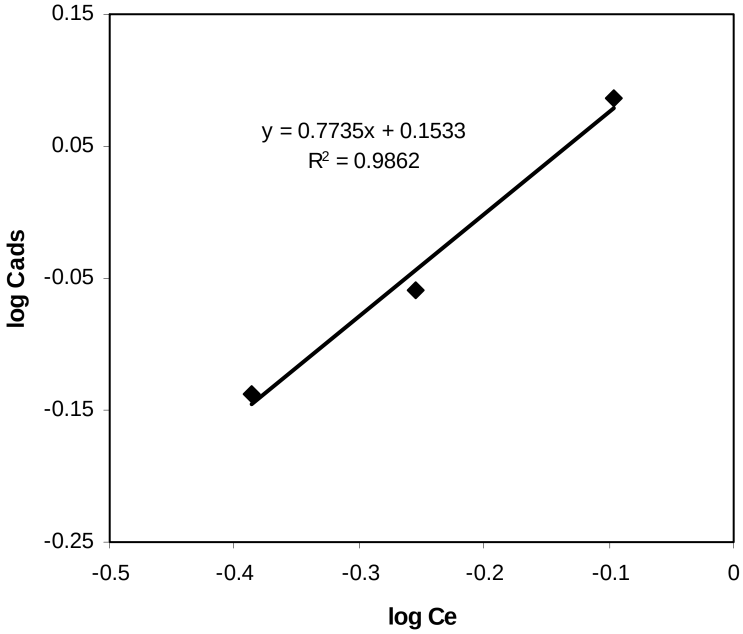

Figure 72: Freundlich isotherm model for adsorption of Cd(II) onto NLP

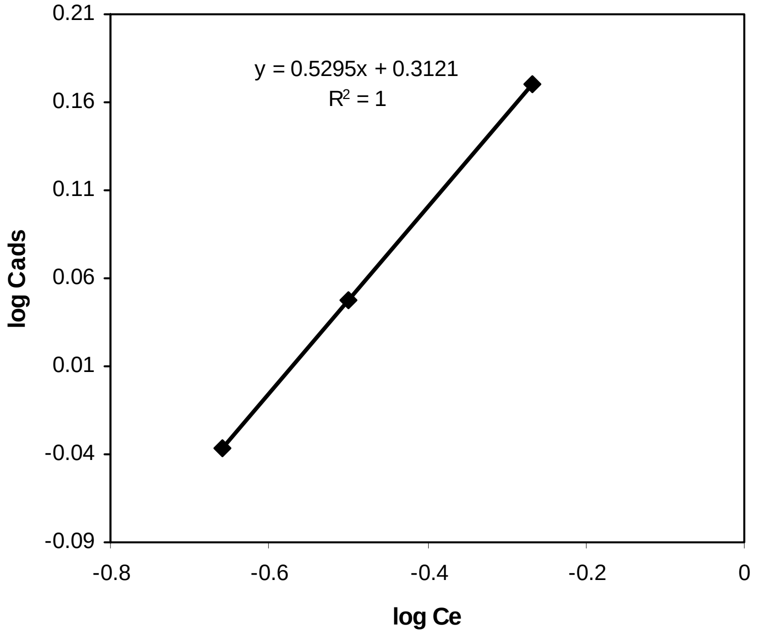

Figure 73: Freundlich isotherm model for adsorption of Cd(II) onto JSP

4.2.3. Chromium

4.2.3.1 Effect of Contact Time and Initial Metal ion Concentration

The experimental results of adsorptions at various Cr(III) ion concentrations of 1.17, 2.03, and 9.34 mg/L with contact time were shown in Figures 74, 75 and 76 JSP, NSP and NLP, respectively. The equilibrium data reveal that, the percent adsorption decreased with decrease in initial Cr(III) ion concentration. Equilibrium has established at six hours for all concentrations. Figures 74, 75 and 76 reveal that the curves are single, smooth, and continuous, leading to saturation, suggesting the possible monolayer coverage of the Cr(III) ions on the JSP, NSP and NLP surface.

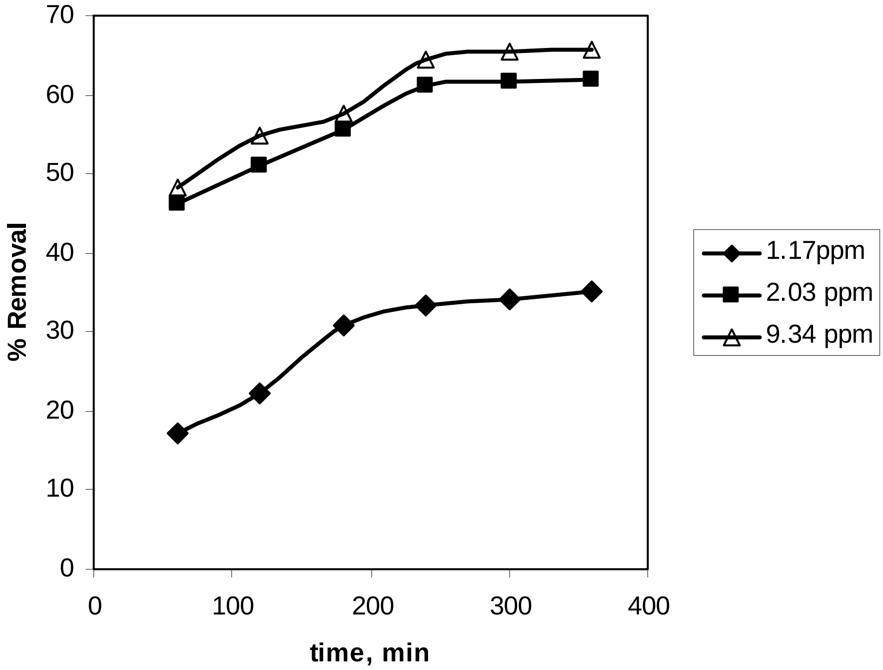

Figure 74: % of Cr(III) Removal vs Contact time with 1.0g JSP at pH 6-7

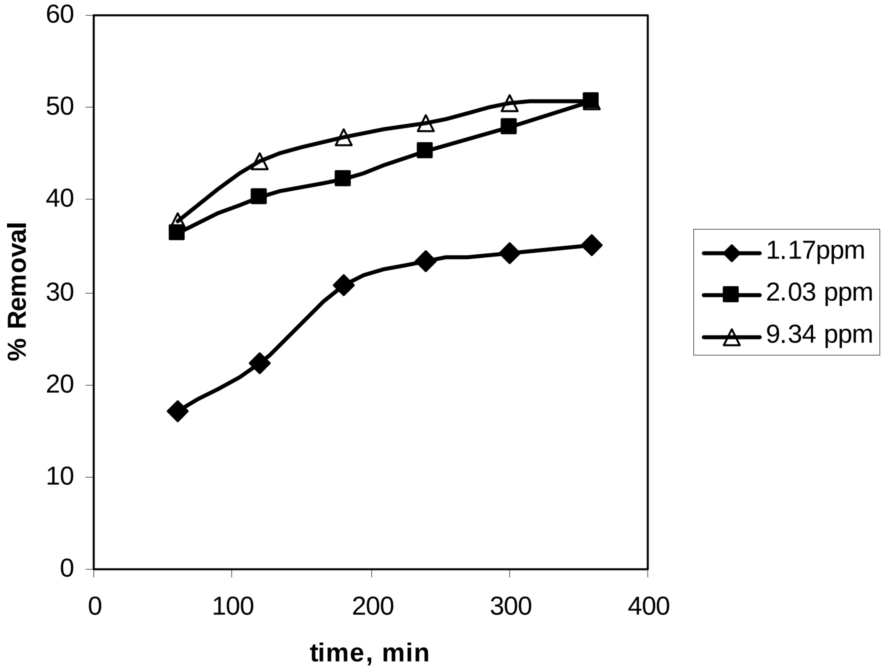

Figure 75: % of Cr(III) Removal vs Contact time with 1.0g NSP at pH 6-7

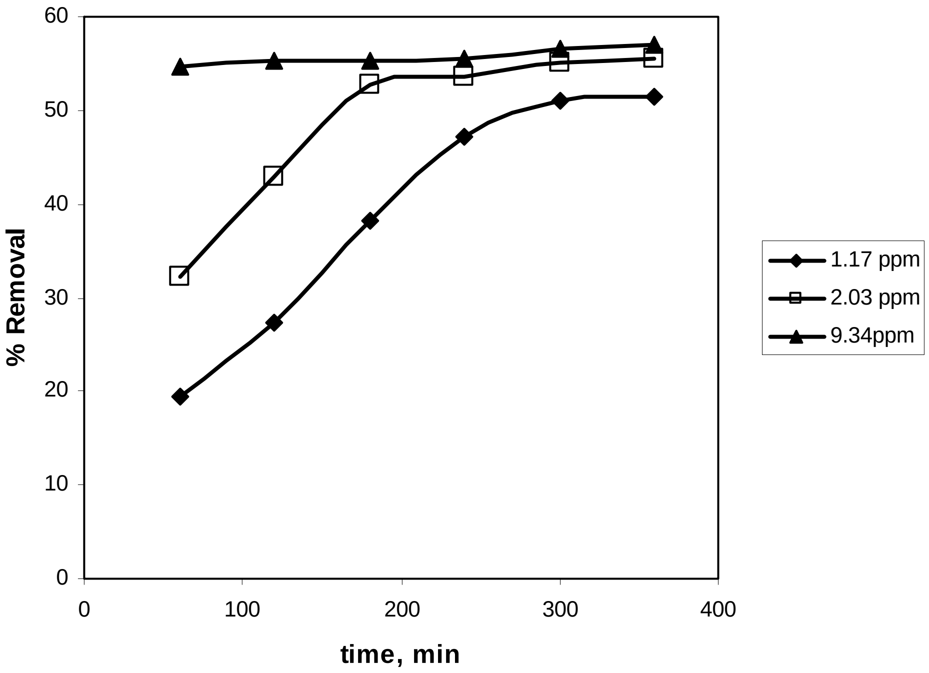

Figure 76: % of Cr(III) Removal vs Contact time with 1.0g NLP at pH 6-7

4.2.3.2 Evaluation of Bio-sorption Efficiency

The biosorption data for the removal of Cr(III) was correlated with Langmuir and Freundlich models [116]. The Langmuir equation (Eq.1) is valid for monolayer sorption on a surface containing a limited number of sites, predicting a homogeneous distribution of sorption energies.

Using the Langmuir equation (Eq.1), the linear plots of $1/C_{ads}$ versus $1/C_e$ suggest the applicability of the Langmuir isotherm is shown in Figures 77, 78 and 79 for JSP, NSP and NLP, respectively.

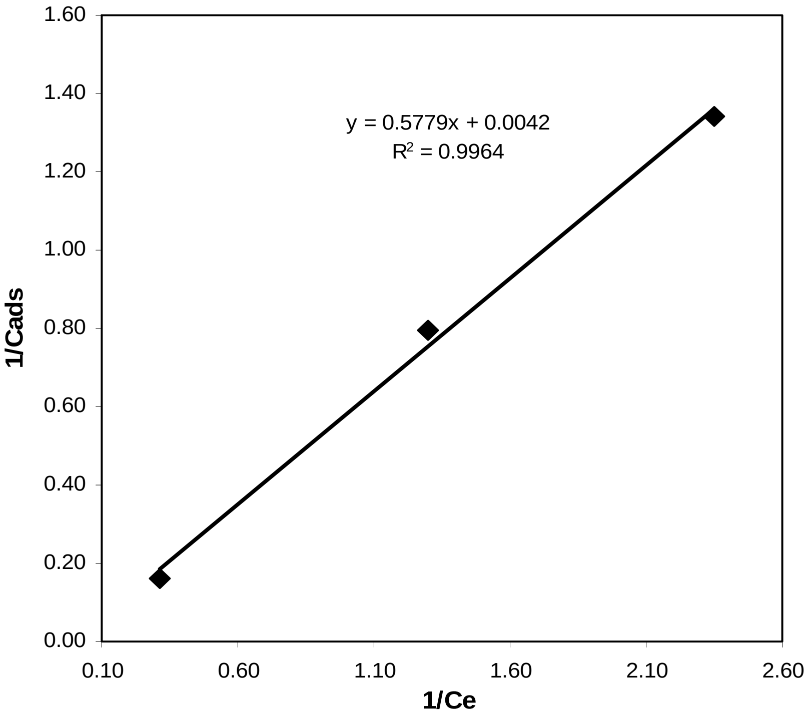

Figure 77: Langmuir isotherm model for adsorption of Cr(III) onto JSP

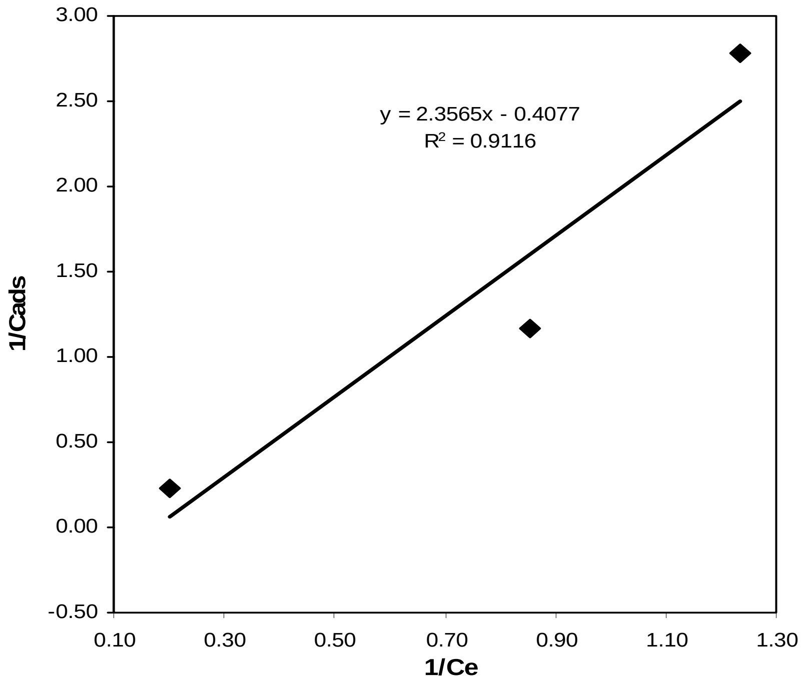

Figure 78: Langmuir isotherm model for adsorption of Cr(III) onto NSP

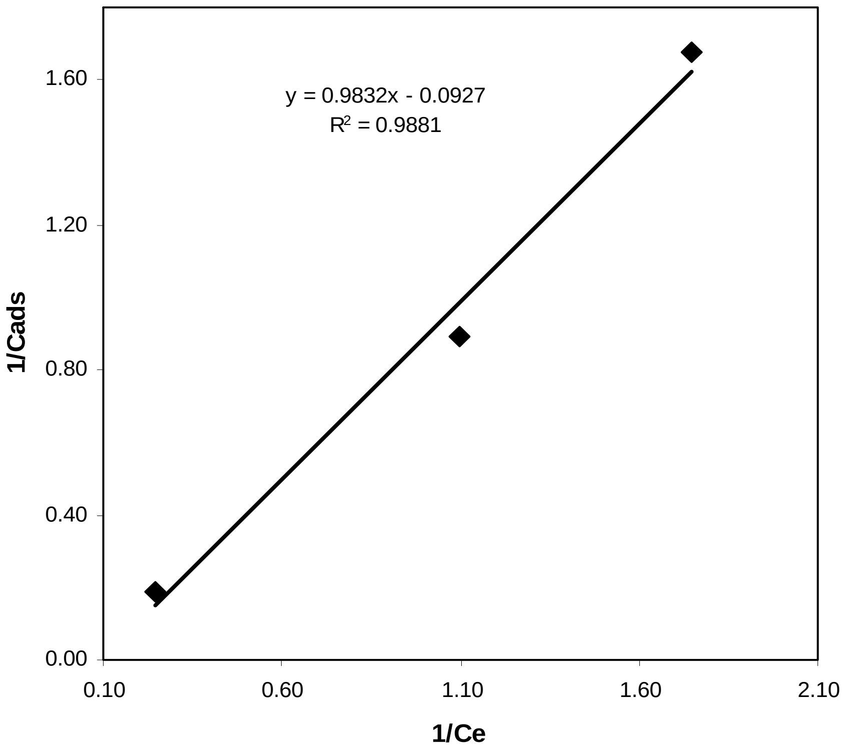

Figure 79: Langmuir isotherm model for adsorption of Cr(III) onto NLP

The Freundlich equation (Eq.2) was also employed for the adsorption of Cr(III) ions on different adsorbent. Linear plots of log C_{ads} versus log C_e correlate with Freundlich isotherm (Figures 80, 81 and 82).

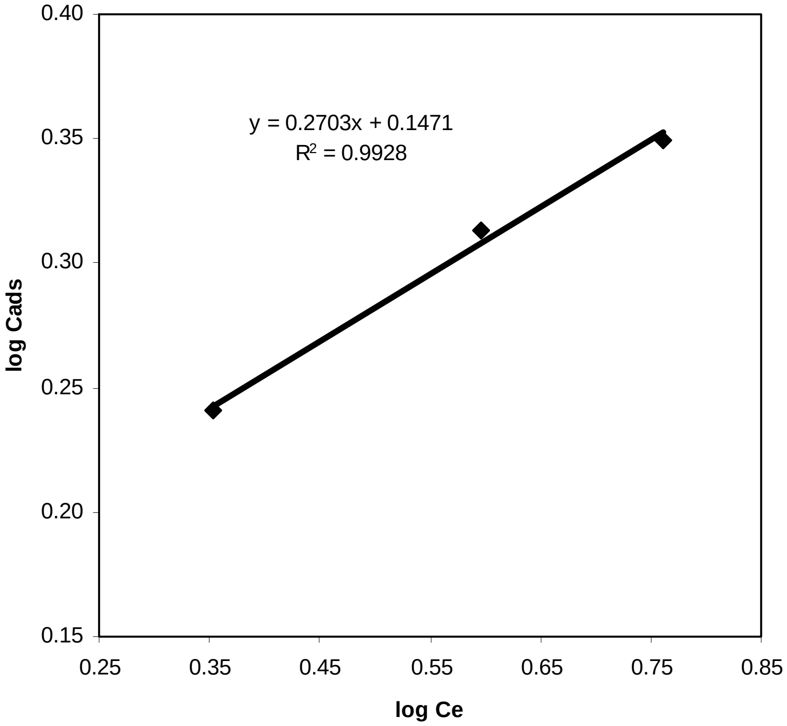

Figure 80: Freundlich isotherm model for adsorption of Cr(III) onto JSP

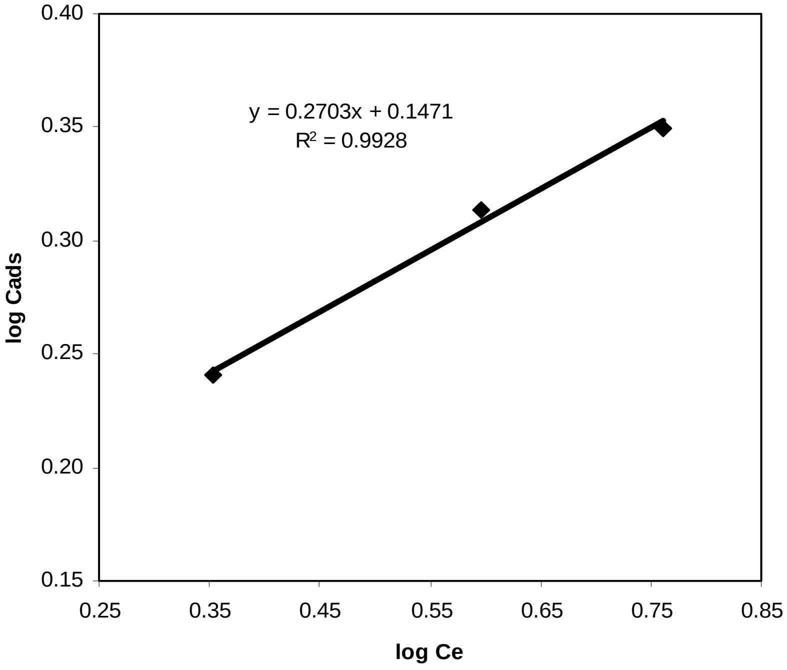

Figure 81: Freundlich isotherm model for adsorption of Cr(III) onto NSP

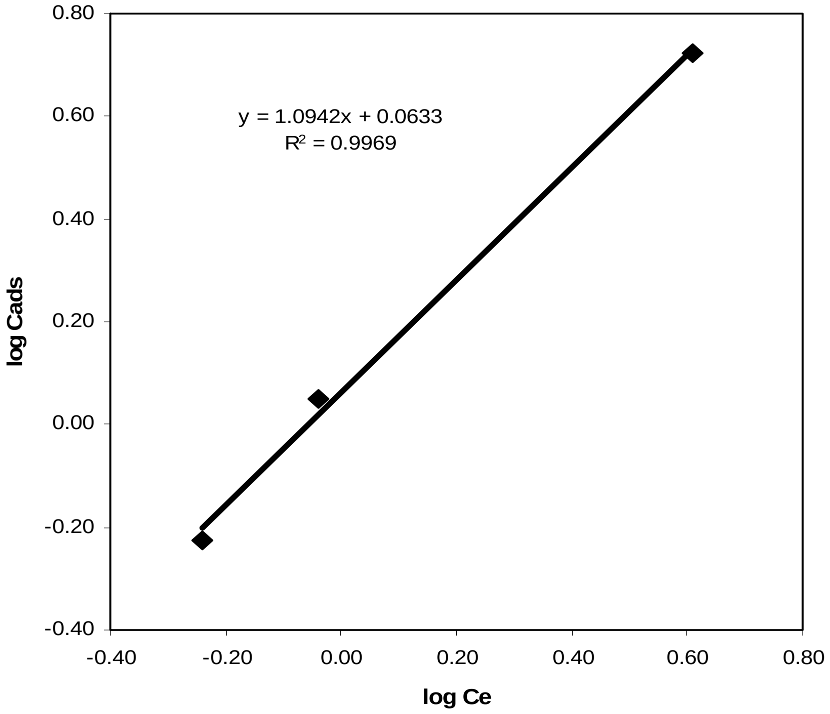

Figure 82: Freundlich isotherm model for adsorption of Cr(III) onto NLP

5. Conclusions

Our goal was to find a process for the removal of Pb(II), Cd(II) and Cr(III) ions from industrial wastewater, which would be easier, readily available and better from the economic point of view compared to the other processes. NLP, NSP and JSP are very effective adsorbent for the removal of toxic metal ions such as Pb(II), Cd(II) and Cr(III) even when their concentration is as low as 4 ppm. These bio-adsorbents are cheap, abundant and above all biodegradable. Furthermore the adsorbents show maximum removal capacity at pH 6. This indicates that no additional reagent is required to control the pH of the medium. So, they may be replaced most conventional adsorbents in the removal and recovery of metal ions from industrial wastewater. From the results, it is possible to conclude that:

- The experimental data produces good fits with both Langmuir and Freundlich isotherms and the adsorption coefficients agree well with the conditions supporting favorable adsorption.

- Neem leaf powder (NLP), Nut shell powder (NSP) and Jute stick powder (JSP) have very good potential for utilization as an adsorbent for Pb(II) and Cd(II) from aqueous medium. But for Cr(III), they show less potential adsorption capacity. Above 95% Pb(II) and Cd(II) can successfully be removed by using NLP, NSP and JSP as adsorbents.

- The kinetics of adsorption of Pb(II), Cd(II) and Cr(III) on NLP, NSP and JSP are complex and while the results were tested with models based on pseudo first order and Pseudo second order equation, close conformity could be obtained with pseudo second order mechanism.

- The adsorption is influenced by pH of the medium, initial concentration of the metal ions and the amount of the adsorbent.
- The adsorption process is spontaneous at room temperature and normal pressure.
- Desorption studies indicate that hydrochloric acid is a better reagent than deionized water for desorption Pb(II), Cd(II) and Cr(III) ions from NLP, NSP and JSP.

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Appendix A

Langmuir Adsorption Isotherm:

Calculation:

Langmuir Equation

$$\frac{1}{C_{ads}} = \frac{1}{K_L bC_e} + \frac{1}{K_L}$$

This is a straight line equation e.g; $y = mx + C$

From the experimental data, $y = 0.088x + 0.0072$ [for Cd (II) on NLP]

Intercept (c), $\frac{1}{K_L} = 0.0072$

$$K_L = 138.89 mg/g$$

$$= 138.89 \ x \ \frac{10^{-3} g}{g}$$

$$= 138.89 \ x \ \frac{10^{-3}}{} \frac{10^{-3} kg}{10^{-3} kg}$$

$$= 138.89 \ x \ \frac{10^{-3} kg}{kg}$$

$$= 1.39x10^{-3} kg/kg$$

Slope (m), $\frac{1}{K_L b} = 0.888$

$$b = 0.0818182 L/mg$$

$$= 81.82 \; x \; \frac{10^{-3} m^3}{10^{-6} kg}$$

$$= 81.82 \; x \; \frac{10^{+3} m^3}{kg}$$

$$[\because 1L = 1000 \; cm^3 = 0.1 x 0.1 x 0.1 m^3$$

$$= 10^{-3} m^{3\,3}] \; And \; [mg = 10^{-3} g = 10^{-6} kg]$$

$$\therefore b = 81.82 m^3/kg$$

Appendix B

Freundlich Isotherm:

Calculation:

$$\text{Equation: } \log C_{ads} = \log K_f + \frac{1}{n} \log C_e$$

This is a straight line equation.

From the experimental data: $y = 0.9512x + 1.0222$ [for Cd(II) on NLP]

Intercept(c), $\log K_f = 1.0222$

$$K_f = 10.524 mg/g = 10.524 \; x \; \frac{10^{-6} kg}{10^{-3} kg}$$

$$= 10.524 \; x \; \frac{10^{-3} kg}{kg}$$

$$= 1.0524 \; x \; \frac{10^{-2} kg}{kg}$$

Slope (m), $\frac{1}{n} = 0.9512 (L/g)$

$$n = 1.0513 (g/L)$$

$$= 1.0513 \; x \; \frac{10^{-3} kg}{10^{-3} m^3}$$

$$= 1.0513 kg/m^3$$

Appendix C

Dimensionless factor, $R_L = \frac{1}{1+bc_0}$

4ppm = 4 mg/L

$$= \frac{4x10^{-6} kg}{10^{-3} m^3}$$

$$= \frac{4x10^{-3} kg}{m^3}$$

$$\therefore 6ppm = \frac{6x10^{-3} kg}{m^3}$$

$$\therefore 8\ ppm = \frac{8x10^{-3} kg}{m^3}$$

$$\therefore 10\ ppm = \frac{10\ x10^{-3} kg}{m^3}$$

So, Dimensionless factor, $R_L \quad \frac{1}{1 + \frac{81.82\ m^3}{kg} x \frac{4\ x\ 10^{-3}\ kg}{m^3}}$

[Here, b = 81.82 m^3/kg and C_0 = 4ppm = $\frac{4x10^{-3} kg}{m^3}$]

$\therefore R_{L1}$= 0.753

$\therefore R_{L2}$= 0.67

$\therefore R_{L3}$= 0.60

$\therefore R_{L4}$= 0.55

Determination of Free Energy, ΔG^0

From the experimental data for Cadmium:

Total Conc.	C_{solid}	C_{liquid}
4ppm	3.6672	0.3328
6ppm	5.5023	0.4977

8ppm	7.3155	0.6845
10ppm	9.1349	0.8651

Equilibrium constant, $K_0 = \frac{C_{solid}}{C_{liquid}}$

For 4ppm,

K_1 = 3.6672/0.3328 = 11.02

logK_1 = log (11.02) = 1.0422

Free energy, ΔG^0 = (-2.303) RT logK_0

[Here, R = 8.314472 J/mol.K

And T = 25^0C = (273+25) K= 298K]

$$\Delta G^0 = (-2.303)x(8.314\tfrac{J}{mol})x(298K)x(1.0422)$$

= -5946.97 J/mol

= - 5.947 kJ/mol

For 6ppm,

ΔG^0 = - 5706.1722 x 10438 = -5956.1026 J/mol = 5.956 kJ/mol

For 8ppm,

ΔG^0 = -5.867 kJ/mol

For 10ppm,

ΔG^0 = -5.841 kJ/mol

Appendix D

Pseudo first-order equation

Pseudo first-order equation is generally expressed as:

$$\log\left(C_e - C_t\right) = \log\left(C_e\right) - \frac{k_1}{2.303}t$$

log ($C_e - C_t$) vs t is a straight line and k_1 and C_e can be determined from the slope and intercept of the plot, respectively.

Cd (II) adsorption onto JSP**:**

From the experimental data, $y = 0.0036x + 0.0949$

Slop, $k_1/2.303 = 0.0036$

$\therefore k_1 = (0.0036) \times 2.303 = 0.0083$

And log$Ce = 0.0949$

$\therefore Ce = 1.2442$

Pseudo second-order equation

Pseudo second-order adsorption kinetic rate equation is expressed as:

$$\left(\frac{t}{C_t}\right) = \frac{1}{k_2 C_e^2} + \frac{1}{C_e}(t)$$

If the initial adsorption rate, h (mg·g^{-1}·min^{-1}) is:

$$h = k_2 C_e^2$$

Then the Eqs. becomes:

$$\left(\frac{t}{C_t}\right) = \frac{1}{h} + \frac{1}{C_e}(t)$$

This is a straight line equation from which C_e and k_2 can be determined from the slope and intercept of the plot, respectively.

From the experimental data, $y = 0.2674x + 3.7442$ [Adsorption of Cd(II) on JSP]

Slop, $1/Ce = 0.2674$

$\therefore Ce = 3.73397$

Intercept, $1/h = 3.7442$

$\therefore h = 0.2671$

$k_2 = h / C_e^2$

$\therefore k_2 = 0.0191$

Table: Equilibrium data for the adsorption of Cadmium on to NLP, NSP and JSP

Contact time (min)	Initial Conc. C_o mg/L	Equilib Conc. C_e mg/L (NLP)	Equilib Conc. C_e mg/L (NSP)	Equilib Conc. C_e mg/L (JSP)
120		1.0196	1.0198	1.4796
180		0.9309	0.9312	1.1009
240		0.8979	0.8978	1.0979
300		0.8651	0.8891	0.9951
360		0.8650	0.8995	0.9905
60	4.0	0.3996	0.7393	0.8196
120		0.3896	0.6491	0.6896
180		0.3648	0.5248	0.5648
240		0.3495	0.4295	0.4995
300		0.3328	0.3841	0.4328
360		0.3324	0.3524	0.3724
60	6.0	0.5948	0.7848	1.3248
120		0.5613	0.6613	0.9913
180		0.4998	0.5998	0.7498
240		0.4986	0.5126	0.6586
300		0.4977	0.5085	0.6277
360		0.4974	0.5067	0.6074
60	8.0	0.8254	0.9653	1.7254
120		0.7419	0.8419	1.2219
180		0.7075	0.7173	0.8075
240		0.7016	0.7026	0.7016
300		0.6845	0.6845	0.6845
360		0.6840	0.7081	0.7744
60		1.1052	1.1053	2.0052

Table: Equilibrium data for the adsorption of Lead on to NLP, NSP and JSP

Contact time (min)	Initial Conc. C_o mg/L	Equilib Conc. C_e mg/L (NLP)	Equilib Conc. C_e mg/L (NSP)	Equilib Conc. C_e mg/L (JSP)
60	4.0	0.4053	0.4229	0.2432
120		0.3118	0.3087	0.2184
180		0.3119	0.3025	0.1832
240		0.2673	0.2801	0.1612
300		0.2544	0.2781	0.1497
360		0.2524	0.2778	0.1192
60	6.0	0.5331	0.5614	0.5015
120		0.4576	0.5132	0.4402
180		0.3087	0.4302	0.4031
240		0.2478	0.3621	0.3609
300		0.2483	0.3437	0.2702
360		0.2489	0.3211	0.2057
60	8.0	0.7334	0.6596	0.8540
120		0.6023	0.6351	0.7244
180		0.4561	0.4413	0.6417
240		0.3354	0.3027	0.5791
300		0.3337	0.2982	0.5033
360		0.3326	0.3007	0.4397
60	10.0	1.1464	1.0153	1.5023
120		0.9846	0.8433	1.5011
180		0.8867	0.6751	1.4819
240		0.6919	0.5834	1.1457
300		0.6036	0.5001	1.0191
360		0.6251	0.4137	0.9632

Table: Equilibrium data for the adsorption of Chromium on to NLP, NSP and JSP

Contact time (min)	Initial Conc. C_o mg/L	Equilib Conc. C_e mg/L (NLP)	Equilib Conc. C_e mg/L (NSP)	Equilib Conc. C_e mg/L (JSP)
360	4.0	1.9298	1.9883	0.9632
300		1.9334	2.0103	0.9718
240		2.0572	2.1599	1.0645
180		2.2328	2.2324	1.3081
120		2.3219	2.3761	1.5125
60		2.7342	2.4783	2.0043
360	6.0	4.4479	3.3927	1.4943
300		4.4753	3.4809	3.0653
180		4.5967	3.9419	2.0524
60		4.6084	3.6404	1.5056
360	8.0	6.0121	5.8003	1.9324
300		6.0383	5.8172	3.4657
180		6.1976	5.7641	2.7865
60		6.4631	6.0295	2.0038
360	10.0	8.2389	7.9321	2.2925
300		8.2452	7.9743	2.8652
180		8.4475	7.7081	2.4824
60		8.4499	8.1164	2.3653

Poster Presentation:

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