HEAVY METAL IONS REMOVAL FROM AQUEOUS SOLUTION USING CHEMICALLY MODIFIED LIGNOCELLULOSIC MATERIALS (COCONUT BY-PRODUCTS)

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Heavy metal ions removal from aqueous solution using chemically modified lignocellulosic materials (coconut by-products).

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DECLARATION

No portion of the work referred to in this dissertation has been submitted in support of an application for another degree of qualification of this or any other university or institution of higher learning.

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ABSTRACT

Lignocellulosic materials such as coconut by-products are also known as agro-based resources for the cellulose, hemicellulose, lignin and extractives. In Malaysia, coconut tree and products are available everywhere from peninsula Malaysia to Sabah and Sarawak. Hence, coconut by-products were available in abundance and cheaply, for this reason the study of lignocellulosic material derived from coconut by-product for heavy metal ions removal are very important. The high adsorption capacity of lignocellulosic materials derived from the coconut by-product and their potential applications as effective and economical adsorbents for heavy metals removal from aqueous solutions were investigated. The coconut’s husks and leaf have been shown to be equally effective as activated carbon in removing the heavy metal ions such as Pb(II), Cu(II) and Zn(II). The coconut husks had been shown to possess higher heavy metal adsorption capacity compared to that coconut leaf. The modification of the coconut husks and leaf fibre by the tartaric acid shown that there are improved much in the adsorption of heavy metal ions. Both unmodified and modified coconut husks and coconut leaf showed strong and rapid adsorption in the first 15 minutes. All the adsorption reached the equilibrium stage after three hours. It was observed that the adsorption capacity of coconut husks and leaf for the removal of heavy metal ions was being affected by the initial metal ions concentration and solution pH. From the study had been done, the initial metal ions concentration of 300 mg/L and pH 5 were the optimum conditions for adsorption of heavy metal ions from aqueous solutions using coconut husks and leaf as adsorbent materials.
ABSTRAK

1. Introduction

Heavy metal is a large group of trace elements which are important both industrially and biologically (Allanay, 1995). There are 60 heavy metals in this world. These include Aluminium, Arsenic, Beryllium, Bismuth, Cadmium, Chromium, Cobalt, Copper, Iron, Lead, Manganese, Mercury, Nickel, Selenium, Strontium, Thallium, Tin, Titanium, and Zinc. All these heavy metals can cause metabolite anomalies in very high concentrations, but Copper, Nickel, Chromium and Zinc are essential for life at low concentrations.

Now days, the term of ‘heavy’ implies high densities while ‘metal’ is a pure element or an alloy of metallic elements. Metals are chemically known by high thermal and electricity conductivity, high reflectivity and metallic luster, strength and ductility (Masters, 1991). Lignocellulosic materials such as coconut by product have the ability to remove heavy metal ions such as copper, nickel and lead from aqueous solutions (Cindy, 2004) Lignocellulosic naturally contain lignin, cellulose and hemicelluloses which these content make them capable of removing heavy metals ions. Lignocellulosic materials and fiber are low cost unconventional sorbent and have been tested for potential use as heavy metal removal sorbents. Lignocellulosic material’s pollutant absorption ability can be improved by chemical modification. Study showed that saponification and phosphorylation of lignocellulosic materials enhanced their sorption capacities for heavy cationic metals in water (Nada et al., 2002, Romero-Gonzalez et al., 2001).

Coconut is a tropical plant of the Arecales (palmae) family. Three main coconut types exist in this world, tall (C. nucifera typical), dwarf (C. nucifera nana) and hybrids between two. Being one of useful plants in the world, coconut had many applications for daily life. Coconut’s trees are cultivated mainly for the high oil content of the endosperm (copra), which is widely used in both food and non-food industries such as margarine and soap industries. The multiplications of coconut uses make them very important to us. Large production areas are found along the coastal regions in the wet tropical areas of Asia. Generally, coconut can be found in Philippines, Indonesia, India, Sri Lanka, Malaysia and others ASEAN countries.
Coconut husk and leaves are 100% natural biodegradable products. Coconut husk (‘kokos’ of ‘coco’) is the seed hair fibre obtained from the outer shell (endocarp). The fibrous coconut husk is used in many applications including ropes and twines, aquarium filters, car seat covers, flower pots, heat insulation, brushes, matting, rugs, and carpets. The leaves of coconut are also important for weaving into mats, roofs and many other applications. The coconut is more durable than other natural fibres and a complicated regeneration processes unnecessary. Coconut fibre divided into two categories, i.e. Mattress fibre and bristle fibre. Mattress fibre consists of short length fibre, weaker in strength than the bristle fibers. Bristle fibre is longer in length with higher breaking strength than Mattress fibre.

Several adsorbents derived from naturally occurring lignocellulosic wastes have been observed to be efficient in minimizing or reducing the amount of heavy metals such as copper, lead and zinc present in aqueous solutions, these adsorbent gained their respective capacities of adsorption depending on the types of heavy metal ions. The removal of heavy metal ions from aqueous solutions is desirable for minimization, if not prevention of potential hazards in our lovely environments.

The objectives of this study are to evaluate the effectiveness of lignocellulosic for removing heavy metal ions from aqueous solutions. Factors affecting the adsorption capacity of heavy metal ions in aqueous solutions, such as solution’s pH and as well initial metal ions concentration will be investigated.
2. Literature review

2.1 Metal Chemistry and toxicity

Heavy metal has their own characteristic, chemical properties, applications and toxicity to human health and environment. There are three heavy metal want to remove from the aqueous solutions such as lead, copper and nickel. All of this heavy metal is toxic in higher concentrations level. Water pollution cause by heavy metals is a great concern of the worldwide. The heavy metal ions removal processes that occur in natural, domestic and industrial treatment systems are considered to be adsorption, chemical precipitation, and biological treatment.

Lead (Pb) is one of the oldest metals known to man and since medieval times has been used in piping, building materials, soldering, paints, ammunitions and castings. Lead has a bright luster and is a dense, ductile, very soft, highly malleable, bluish-white metal that has poor electrical conductivity. This true metal is highly resistant to corrosion and because of this property, it is used to contain corrosive liquids such as sulfuric acid, H₂SO₄. Lead can be toughened by adding a small amount of antimony or other metals to it. Native lead does occur in nature but it is rare. Currently lead is usually found in ore with zinc, silver and copper and is extracted together with these metals. The main lead mineral is galena (PbS), which contains 86.6% of lead.

In mining, the ore is extracted by drilling or blasting and then crushed and ground. The ore is then treated using extractive metallurgy. The Froth flotation process separates the lead and other minerals from the waste rock (tailings) to form a concentrate. The concentrate, which can range from 50% to 60% lead, is dried and then treated using pyrometallurgy. The concentrate is sintered before being smelted in to produce a 97% lead concentrate. The lead is then cooled in stages which cause the lighter impurities (dross) to rise to the surface where they can be removed. The molten lead bullion is then refined by additional smelting with air being passed over the lead to form a slag layer containing any remaining impurities and producing 99.9% pure lead.
Lead has four stable, naturally occurring isotopes: Pb-204 (1.4%), Pb-206 (24.1%), Pb-207 (22.1%) and Pb-208 (52.4%). Pb-206, Pb-207 and Pb-208 are all radiogenic, and are the end products of complex decay chains that begin at U-238, U-235 and Th-232 respectively. The corresponding half-lives of these decay schemes vary markedly: $4.47 \times 10^9$, $7.04 \times 10^8$ and $1.4 \times 10^{10}$ years, respectively. Each is reported relative to $^{204}$Pb, the only non-radiogenic stable isotope. The ranges of isotopic ratios for most natural materials are 14.0-30.0 for Pb-206/Pb-204, 15.0-17.0 for Pb-207/Pb-204 and 35.0-50.0 for Pb-208/Pb-204, although numerous examples outside these ranges are reported in the literature.

More recently, Pb has been used mainly in storage batteries (35%), in gasoline as tetraethyl lead (5% but is continuously decreasing), capable covering (10%) and chemicals (15%) (Demayo et al., 1984). Lead is a member of group IVB of the Periodic Table and has atomic number 82. There are 2 stable oxidation of lead, namely Pb (II) and Pb(IV). In environment, Pb(II) is the dominant species. Elemental Pb density is 11.3 pg/cm$^3$, boiling point at 1744°C and is blue grey in colour and smelts at 327 Celsius.

Studies in vitro and in vivo have shown that Pb concentrations as low as 0.2 mg/L can cause adverse affects in aquatic biota (Wong et al., 1978). Lead as a pollutant has assumed particular importance due to its relatively high toxicity to human, especially brain retardation in children. Environmental exposure to low levels of Pb has been associated with the wide range of metabolite disorders and neuropsychological deficits, especially in children (Ngiagu, 1978; Silvany-Neto, et al., 1989). Lead is a poisonous metal that can damage nervous connections (especially in young children) and cause blood and brain disorders. Long term exposure to lead or its salts (especially soluble salts or the strong oxidant PbO$_2$) can cause nephropathy, and colic-like abdominal pains.

Lead occurs in the environment in a wide range of physical and chemical forms which greatly influence its behavior and its effects on the ecosystem. Most of the Pb in the environment is in the organic form. In addition, Pb is also present in the organic form such as alkyl Pb from auto emissions. The size of particulates containing Pb significantly influences the aerial transport and its ecology effects. In aqueous solutions, Pb is
predominant associated with the suspended particulates and tends to accumulate in the sediments (Zabel, 1989).

Nickel is a member of group VIII in periodic Table. Nickel have oxidation number such as Ni(I), Ni(II), Ni(III), and Ni(IV) but Ni(II) is more stable over a wide range of pH and redox condition. The salts of nickel are slightly acidic. Nickel is an essential element but the levels required by plants and animals are very low. At higher concentrations, it is known to be toxic to both plants and animals, whereas at very high levels of exposure, nickel salts are known to be carcinogenic (Smith et al., 1997). Nickel is ingested by human beings through the consumption of plants and animals that contain nickel. Nickel levels were determined using FAAS in foods in the Netherlands by Ellen et al. (1978). They were found to be less than 0.5 mg/kg fresh weight in most products, except for cacao products and nuts, which contained nickel levels of up to 9.8 and 5.1 mg/kg respectively. Smart & Sherlock (1987) reported that nickel levels, determined using FAAS in meat, fruit, and vegetables were of the order of more than 0.2 mg/kg fresh weight. Aquatic organisms, e.g., mollusks and fish, may contain relatively large amounts of nickel, if the nickel concentration in the water is high.

In fact, nickel levels in drinking-water mostly below 10 μg/litre (Clemente et al., 1980). Leaching processes from water taps and fixtures contribute to nickel levels already present in drinking-water. Between 18 and 900 mg of nickel were leached from 10 used water taps, which had been filled, in an inverted position, with 15 ml deionized water, and left overnight for 16 hours (Strain et al., 1980). In Denmark, levels of up to 490 μg/litre were observed, when water was left standing overnight in nickel-containing plumbing fittings (Andersen et al., 1983). In areas where nickel is mined, as much as 200 μg nickel/litre has been recorded in drinking-water (McNeely et al., 1972). Assuming a daily intake of 1.5 litres water and a level of 5-10 μg nickel/litre, the mean daily intake of nickel from water for adults would be between 7.5 and 15 μg.
Nickel was found in rocks, air, water, fossil fuels and soils. Most nickel occurs in the ferromagnesium minerals of igneous and metamorphic rocks, such as olivine. Normal nickel concentrations in igneous rocks range from 2 to 60 mg/kg in acidic rocks, 50-200 mg/kg in basic rocks, and 10-2000 mg/kg in ultramafic rocks (Boyle, 1981). The most commercially important nickel ore deposits are accumulations of nickel sulfide minerals in ultramafic igneous rocks. Such deposits are found in Australia, Canada, and the USSR. The ores are composed almost entirely of pentlandite [(Fe,Ni)₉S₈], chalcopyrite (CuFeS₂), and pyrrhotite (Fe₇S₈), and usually contain 1-4% nickel (Duke, 1980). Other nickel ore deposits are formed by the weathering of ultramafic ferromagnesium silicate rocks in humid tropical areas. The residual soil (laterite) developing during the weathering process may contain up to 10 times the amount of nickel in the original rock (Duke, 1980). The nickeliferous lateritic weathering profile is characterized by two deposits, an upper oxide zone and a silicate zone where both varying in proportion. The oxide zone is composed of iron oxides containing nickel in solid solution. In the silicate zone, also called the garnierite zone, nickel is found in the mineral serpentine Mg₃Si₂O₅(OH)₅ substituting for magnesium. The nickel content of lateritic ores is approximately 1-3% (Duke, 1980). Important deposits are located in Brazil, Cuba, Dominican Republic, Guatemala, Indonesia, New Caledonia, and the Philippines.

In glacial areas, nickel-containing components may have been dispersed over wide areas; thus, the nickel contents of the soil can differ considerably from the nickel content of the underlying bedrock. In unweathered glacial sediments, nickel occurs in the same mineral phases as those in which it is found in the rocks, i.e., sulfides and silicates. Weathering of rocks and soils leads to nickel release from nickeliferous minerals. The nickel released is largely retained in the weathered material in association with clay particles and therefore not considered to be very mobile in the superficial environment (Duke, 1980). Nickel can exist in soils in several forms (Hutchinson et al., 1981) including inorganic crystalline minerals or precipitates, complexed or adsorbed cation surfaces and water soluble, free ions or chelated metal complexes in soils or solution. In a soil-water system, nickel may form complexes with inorganic ligands (Cl⁻, OH⁻, SO₄²⁻, or NH₄⁺) (Richter and Theiss, 1980) and organic ligands (humic or fulvic acids) (Nriagu,
Agricultural soils of the world contain between 3 and 1000 mg nickel/kg (NAS, 1975). In forest floor samples collected from 78 sites in 9 states in the northeastern USA, nickel was present at concentrations in the range of 8.5-15 mg/kg (Friedland et al., 1986).

Nickel occurs in aquatic systems as soluble salts adsorbed on clay particles or organic matter (detritus, algae, bacteria) or associated with organic particles such as humic and fulvic acids and proteins. Nickel may enter surface waters from three natural sources (Boyle, 1981) as particulate matter in rainwater, through the dissolution of primary bedrock minerals, and from secondary soil phases. The fate of nickel in freshwater and sea water is affected by several factors including pH, ionic strength, type and concentration of organic and inorganic ligands, and the presence of solid surfaces for adsorption (Snodgrass, 1980). In natural waters, at a pH range of 5-9, the divalent ion Ni^{2+} \text{(Ni(H2O)_{6}}^{2+})\text{ is the dominant form. In this pH range, nickel may also be adsorbed on iron and manganese oxides, or form complexes with inorganic ligands (OH^{-}, SO_{4}^{2-}, Cl^{-} or NH_{3}) (Richer & Theiss, 1980). If sulfate concentrations are sufficiently high, nickel sulfate may be the predominant soluble form and under anaerobic conditions, sulfide is the major factor controlling the solubility of nickel (Richer & Theiss, 1980). Nickel concentrations of 0.228-0.693 µg/litre, determined for a vertical open-ocean water profile, were considered to reflect the actual nickel concentration in this medium (Bruland et al., 1979). Concentrations of nickel in freshwater systems are generally less than 2-10 µg/litre (Stokes, 1981).

Atmospheric nickel is considered to exist mainly in the form of aerosols with different nickel concentrations in particles depending on the type of source (Schmidt & Andren, 1980). Major natural sources include the aerosols constantly produced by the oceanic surface, windblown soil dusts, and volcanic ash. Nickel is released from plants during growth at different levels depending on soil composition. Forest fires produce nickel-containing smoke particles. A part of atmospheric nickel originates from meteoric dusts. Atmospheric nickel concentrations for remote areas that are considered to be relatively free from man-made nickel emissions are in the range of <0.1-1 ng/m³ (marine) and 1-3 ng/m³ (continental) (Schmidt & Andren, 1980). The wide variation in
ambient nickel concentrations reflects the influence of nickel emissions from distant sources being transported by means of meteorological processes. Nickel from natural sources, excluding volcanic dust and forest fires, is probably in the form of the oxide (Barrie, 1981).

Copper is the member of group 1B in Periodic Table. Copper is insoluble in acids but it is readily soluble in oxidizing acids such as nitric acid and sulphuric acid. The oxidation number of copper is Cu(I) and Cu(II). Copper is an essential element for all living organisms. It plays a catalytic role for many enzyme systems, perhaps the most notable of which are the enzymes cytochrome oxidase and the electron carrier plastocyanin (Coale and Bruland, 1998; Flemming and Trevors, 1989). Copper toxicity, especially to aquatic organisms determined by the chemical forms in which it is present. There is general consensus among biologist that free cupric ion, Cu²⁺, is the most biotoxic form of Cu in natural wastes (Crecelius et al., 1982; Flemming and Trevors, 1989; Sander et al., 1983; Sunda and Guillard, 1976; Sunda et al., 1984).

Copper salts such as copper sulphate are gastric irritants and produce corrosion of the gastric and intestinal epithelium. Patel et al. (1976) suggested that since the Cu(II) ion is a strong oxidising agent it will oxidise oxyhaemoglobin from the ferrous to the ferric form. In this form, haemoglobin loses its oxygen-binding capacity resulting in methaemoglobinemia and cyanosis (Chugh et al., 1975; Patel et al., 1976; Thirumalaikolundusubramaniam et al., 1984; Nagaraj et al., 1985). Furthermore, the restoration of haemoglobin to the ferrous form depends on the transfer of electrons from NADH, NADPH and reduced glutathione. Glucose-6-phosphate dehydrogenase, which has a major function in maintaining the NADPH concentration in the red cell, is inhibited by copper. NADPH is also necessary for maintaining the level of reduced glutathione, which in turn protects the red cell against the haemolytic effects of oxidising substances (Walsh et al., 1977). The inhibition of this enzyme by copper(II) would explain the haemolysis which is commonly observed in cases of acute copper poisoning. Intravascular haemolysis and a direct action of copper on the kidneys often lead to tubular necrosis (Patel et al., 1976).
3. Materials and Methods

3.1 Sample preparation

Coconut husk and leaves were being collected from Kota Samarahan area. The sample was chemically modified based on the method published by Marshall et al., 2001 with some modification. The sample were cleaned with distilled water, grounded to pass through a 1 mm sieve, treated with 1.2 M tartaric acid and then labeled sample 1, sample 2, and so on.

3.2 Metal ions Adsorption studies

The metal ions adsorption study was based on the methods as reported by Seki et al., (1997) and Tieman et al., (2000).

3.3 Preparation of metal ions standard solutions

The standard solutions of lead, Pb(II), Zn(II) and Cu(II) ions were prepared from analytical grade of hydrated metal acetates, Pb(CH$_3$COO)$_2$·3H$_2$O, Ni(CH$_3$COO)$_2$·4H$_2$O and Cu(CH$_3$COO)$_2$·H$_2$O respectively.

A 100mL of 1000 mg/L stock solutions of Pb(II), Ni(II) and Cu(II) ions will be prepared by dissolve 0.1831 g of Pb(CH$_3$COO)$_2$·3H$_2$O, 0.424 g of Ni(CH$_3$COO)$_2$·4H$_2$O and 0.3142 g of Cu(CH$_3$COO)$_2$·H$_2$O, respectively in separate 100 mL volumetric flasks with deionised water. All stock solutions will be acidic by addition of approximately 1 mL of 65% nitric acid (HNO$_3$) and topped up to the mark with deionised water. Standard metal ions solutions with the range of concentrations will be subsequently prepare by separately diluting appropriate volumes of the stock solutions in 100 mL volumetric flasks. All remaining stock solutions will store in refrigerator at the suitable temperature (4°C) for the future use. The concentrations of each metal ion standard solutions will be verifying using Flame Atomic Absorption Spectrometer (Perkin Elmer Model 3110).
3.4 Batch equilibrium study

Glass bottle of 250 mL capacity were filled with 100 mL standard metal ions solutions of 100 mg/L. 0.5 grams of test adsorbents were added to each bottle. The adsorbents were allowed to equilibrate with the metal ion solutions using a reciprocating shaker with the speed of 200 rpm for various equilibrium intervals up to 24 hours at the room temperature. Separation of the adsorbents and solution is carried out by using the filtration using Whatman 41 filter paper. The filtrates collected were analyzed by the atomic absorption spectrometry (AAS). The absorption of the metal ions by the test absorbents was subsequently calculated by the mass balance. Duplicate run were made for each adsorption experiment. Factors that affect the absorption such as pH and initial metal ions concentration were investigated under the same experimental procedures.

3.5 Kinetic adsorption studies

100mL of 100 mg/L standard metal ion solutions was put in glass bottles 250 mL. 0.5 grams of test adsorbents were added into each bottle. The adsorbents were allowed to equilibrate with the metal ion solutions using reciprocating shaker with the speed 200rpm for various equilibrium intervals up to 24 hours at the room temperature. In this study, equilibrate was allowed from 1 minute until 24hours. For the first 60 minutes, kinetic adsorption study was measured at nearly time of shaking. After shake well, samples were separated using filter paper. Filtrate then was dilute into suitable concentration that can be detected by AAS machine. After dilution, the solution concentration was detected by AAS machine to measure the final concentration of adsorption by the selective adsorbent.

3.6 Effect of pH on adsorption studies

100mL of 100 mg/L standard metal ion solutions was put in glass bottles 250 mL. 0.5 grams of test adsorbents were added into each bottle. The adsorbents were allowed to equilibrate with the metal ion solutions using reciprocating shaker with the speed 200rpm for 2 hours with various pH from pH 3 to pH 9. After shake well, samples were separated using filter paper. Filtrate then was dilute into suitable concentration that can be detected by AAS machine. After dilution, the solution concentration was detected by AAS machine to measure the final concentration of adsorption by the selective adsorbent.
3.7 Effect of metal ions initial concentration on adsorption studies

100mL of 100 mg/L standard metal ion solutions was put in glass bottles 250 mL. 0.5 grams of test adsorbents were added into each bottle. The adsorbents were allowed to equilibrate with the metal ion solutions using reciprocating shaker with the speed 200rpm for 2 hours with various metal ions initial concentration from 50 mg/L to 800 mg/L. After shake well, samples were separated using filter paper. Filtrate then was dilute into suitable concentration that can be detected by AAS machine. After dilution, the solution concentration was detected by AAS machine to measure the final concentration of adsorption by the selective adsorbent.

For all dilution process was done by using simple formula of dilution shown as below;

\[ M_1V_1 = M_2V_2 \]

Where,
- \( M_1 \) = initial concentration of solution (mg/L)
- \( V_1 \) = initial volume of solution (mL)
- \( M_2 \) = final concentration of solution (mg/L)
- \( V_2 \) = final volume of solution (mL)
4.0 Result and discussion

4.1 Chemical characteristic

Figure 4.1 show the FTIR peaks for tartaric acid compound. Figure 4.1 show FTIR spectrum for tartaric acid. In this compound, the characteristic peaks of major functional group occurred at 3408 cm\(^{-1}\), (COOH), 3300-3400 cm\(^{-1}\), (OH), (C=O)1738 cm\(^{-1}\), C-O, 1264 cm\(^{-1}\) and bending OH at 1131 cm\(^{-1}\).

![FTIR spectrum for Tartaric Acid](image)

Figure 4.1: The FTIR spectrum for the Tartaric Acid
Figure 4.2 shows the FTIR spectrum for unmodified and modified coconut leaf. Figure 4.2 (a) shows for unmodified coconut leaf, no peaks was observed at 1735 cm$^{-1}$ and 1309-1339 cm$^{-1}$. For figure 4.2 (b), the major characteristic peaks occurred at 1735 cm$^{-1}$ (C=O) and 1309-1339 cm$^{-1}$ (C-O). Both peaks showed evidences that chemical modification coconut leaf happened.

(a)

Figure 4.2 show the spectrum for (a) unmodified and (b) modified coconut leaf.
Figure 4.3 shows the FTIR spectrum for unmodified and modified coconut husks. A major peak was occurring from the cellulose compound. Tartaric acid modification were added (C=O) into coconut husks.

Figure 4.3: The FTIR spectrum for unmodified and modified coconut husks.
4.4 Batch equilibrium Experiment

The absorption capacities of heavy metal ions using coconut's husks from aqueous solution were determined in batch wise condition using 100mg/L (100ppm) of standard solutions metal acetates respectively. The decline in the concentration of the metal ions was determined at various equilibration intervals and these results were compared with the commercial Activated Carbon.

Figure 4.41-4.43 shows the kinetic adsorption of heavy metal ions (Pb$^{2+}$, Cu$^{2+}$ and Zn$^{2+}$) by various adsorbents. Figure 4.41(a) show the adsorption kinetic of Pb$^{2+}$ ions by the unmodified, modified coconut husks and activated carbon. The adsorption curves for all the absorbent were strong during the first 1 minute, then increasing slowly before finally reached the equilibrium stage within 3 hours. The kinetic study was done until 24 hours. Result shows that from the experiment time of 3 until 24 hours, the adsorption of metal ions were constant. This was because the active site of the adsorbent was already full adsorbed with the heavy metal ions.

Figure 4.41(b) show the adsorption kinetic of Pb(II) ions by the varied adsorbents for the first 60 minutes. It show the adsorption of Pb(II) ions was strong and rapid before reached equilibrium within 10 minutes. Commercial activated carbon show the highest adsorption (21.97mg/g) compared to others adsorbents. The modified coconut husks showed the lowest adsorption with the maximum adsorption capacities of 10.87mg/g.
Figure 4.41: The adsorption kinetic of Pb(II) ions by unmodified and modified coconut husks and activated carbon (a) 24 hours and (b) first 60 minutes.

Figure 4.42(a) show the adsorption kinetic of the Cu$^{2+}$ ions by the unmodified, modified coconut husks and commercial activated carbon. The graph showed the rapid adsorption in the first 3 minutes and slowly increased until the equilibrium was reached at about 3 hours. Activated carbon was observed to show the highest adsorption of Cu(II) ions compared to others adsorbents. The maximum of adsorption of Cu(II) ions by the activated carbon (powder) was 9.01mg/g. The unmodified coconut husks showed the higher adsorption (13.9mg/g) compared to modified coconut husks (7.32mg/g)