HEAVY METAL IONS REMOVAL BY LIGNOCELLULOSICS MATERIALS DERIVED FROM SAGO BARK AND LEAVES

Ling Chian Ye

Bachelor of Science with Honours (Resource Chemistry) 2005
HEAVY METAL IONS REMOVAL BY LIGNOCELLULOSICS MATERIALS DERIVED FROM SAGO BARK AND LEAVES

LING CHIAN YE

This project is submitted in partial fulfillment of the requirements for the degree of Bachelor of Science with Honours (Resource Chemistry)

Faculty of Resource Science and Technology
UNIVERSITY MALAYSIA SARAWAK
2005
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.

Ling Chian Ye
Program of Resource Chemistry
Faculty of Resource Science and Technology
University Malaysia Sarawak
ACKNOWLEDGEMENTS

First of all, I would like to express my utmost gratitude and appreciation to my supervisor, Dr. Pang Suh Cem and co-supervisor, Mdm. Wong Sin Yeng, for their support, guidance, encouragement, advice, and patience throughout my undertaking of this research project.

I am also pleased with the staff and management of Timber Research, Training and Technical Centre (TRTTC) for the apparatus or machine used in this study.

My warmest thanks to all my friends, course mates, and laboratory assistants who were always there to assist and help me whenever I faced problems.

Besides that, I also like to thank my family members for their love, support, understanding, care, and inspirations.

Last but not least, I would like to convey my heartfelt gratitude and appreciation to anyone and organization who has contributed towards the success of this project.
TABLE OF CONTENTS

DECLARATION ii
ACKNOWLEDGEMENTS iii
TABLE OF CONTENTS iv
ABSTRACT IN ENGLISH AND MALAY vii
CHAPTER 1 INTRODUCTION 1
  1.1 Justifications 1
  1.2 Objectives of study 4
CHAPTER 2 LITERATURE REVIEWS 5
  2.1 Environmental and health effects of the heavy metal 5
  2.2 Overview of lignocellulosic materials 7
  2.3 Sago palms and their uses 9
  2.4 Studies on the removal of heavy metal ions 11
CHAPTER 3 MATERIALS AND METHODS 17
  3.1 Materials 17
  3.2 Sample preparation 17
  3.3 Physical and Chemical characterization 18
    3.3.1 Physical characterization 18
    3.3.2 Chemical characterization 18
  3.4 Heavy metal adsorption experiments 19
    3.4.1 Batch equilibrium experiments 19
    3.4.2 Continuous column experiments 20
CHAPTER 4 RESULTS AND DISCUSSION

4.1 Physical characterization 21
4.2 Chemical characterization 23
4.3 Batch equilibrium experiment 26
  4.3.1 Adsorption kinetics 26
  4.3.2 Factors affecting adsorption capacity 30
    4.3.2.1 Effect of particle sizes 32
    4.3.2.2 Effect of pH 34
    4.3.2.3 Effect of initial metal ion concentrations 35
    4.3.2.4 Mixed metal ions solution 39
4.4 Summary of adsorption capacity and ANOVA analysis 40
4.5 Adsorption equilibrium 41
4.6 Kinetic sorption 44
4.7 Continuous column experiment 45

CHAPTER 5 CONCLUSION AND RECOMMENDATIONS 47

BIBLIOGRAPHY 48
APPENDICES

APPENDIX 1 Methodology for Chemical Characterization of Sago Bark and Leaves

APPENDIX 2 Data for Physical or Morphology Characteristic of Sago Bark and Leaves

APPENDIX 3 Data for Batch Equilibrium Experiments

APPENDIX 4 Multiple comparisons of LSD for the significance in the mean between different adsorbent samples (sago leaflet, leaf stalk, and bark) and commercial activated carbon (powder)

APPENDIX 5 Multiple comparisons of LSD for the significance in the mean between different heavy metal ions
Heavy Metal Ions Removal by Lignocellulosics Materials derived from Sago Bark and Leaves

Ling Chian Ye
Resource Chemistry Programme
Faculty of Resource Science and Technology
University Malysia Sarawak

ABSTRACT

Lignocellulosics materials derived from sago bark and leaves are available in abundance and cheaply. In this study, sago leaflet, leaf stalk, and bark were characterized chemically and physically and used in the removal of lead(II), copper(II), and nickel(II) ions from aqueous solutions. Two types of experimental apparatus were being used, equilibrium and column experiments. All the adsorbent samples varied considerably in their adsorption capacities. The metal adsorption capacity of all the adsorbent samples for different metals in both types of experiments were found to be in the order: Pb>Cu>Ni. The effects of solution pH, particle size of adsorbent and initial metal concentrations on the adsorption of heavy metal ions from aqueous solutions were also studied. Heavy metal ions adsorption capacities of all adsorbent samples were observed to be affected by these factors. The adsorption equilibrium data were observed to fit the Freundlich model better than the Langmuir model. Kinetic studies showed that the sorption rates could be described well by the pseudo second-order kinetic equation.

Keywords: lignocellulosics adsorbent, heavy metals, adsorption capacity, equilibrium and column experiments

A BSTRAK


Kata kunci: penjerap lignoselulosik, logam berat, keupayaan menjerap, eksperimen keseimbangan dan kolum
CHAPTER 1: INTRODUCTION

1.1 Justification

The presence of heavy metal ions in rivers, ponds, underground water and other water reservoirs which are important for human use has generated considerable concern in recent years. Although the term 'heavy metals' are not easily defined, it is widely recognized and used for the large group of elements with an atomic density greater than 6 g/cm$^3$ (Philips, 1981). According to Alloway (1990), heavy metal ions are commonly adopted as a group name for the metals and metalloids which are associated with pollution and toxicity. However, some heavy metals ions such as, cobalt, chromium, copper, manganese, and zinc are essential in low but critical concentrations for the normal healthy growth of either plants, animals, or both, although they are toxic at high concentrations (Alloway, 1995).

'Toxic metals' is an alternative term to 'heavy metals' but is rather emotive and applicable only to the non-essential elements, such as lead, cadmium, mercury, arsenic, and uranium; it is not appropriate for biological essential elements. According to SenGupta (2002), this group can be referred to as 'toxic elements' as they are all included in the United States Environmental Protection Agency’s (USEPA’s) list of priority pollutants.

The release of heavy metals into the environment needs to be controlled and reduced to minimize effects on the aquatic life and downstream uses. The use of agricultural and forestry waste products as adsorbents is the most promising alternative methods that are being
investigated because unlike synthetic ion-exchange resins, these by-products are cheap and do not require complex regeneration and conservation (Vazquez et al., 1994). Besides, research data have indicated the potential uses of these agricultural waste materials as an alternative to the expensive commercial ion-exchange resins, for removing toxic metals from contaminated water to acceptable safety limits (Kumar and Dara, 1982). Among those being investigated include: cotton (Roberts and Rowland, 1973) walnut waste (Randall et al., 1974a); peanut skins (Randall et al., 1978); sugar cane waste and onion skin (Kumar and Dara, 1982); coffee grounds (Macchi et al., 1986); tea leaves (Tee and Khan, 1988); apple waste (Maranon and Sastre, 1991); wool fibre (Balkose and Baltacioglu, 1992); green algae and rice hull (Roy et al., 1993); and bark and other cellulosic materials (Randall et al., 1974b; Ruf et al., 1992).

It has been reported that certain lignocellulosic wastes such as nut wastes (Friedman et al., 1972; Waiss et al., 1973), tree leaves (Aoyama et al., 1991), barks (Aoyama et al., 1993), and barley straw (Larsen and Schierup, 1981) effectively adsorb heavy metal ions from aqueous solutions, indicating the potential utility of these materials to remove heavy metal ions from industrial effluents. Among these, barks are especially promising because it is available in large quantities from local sawmills. However, several barks bled excessive color into the contacting water. A similar problem occurs with peanut skins (the thin red pellicle covering the meat) and this problem is solved by contacting the skins with dilute formaldehyde in an acid medium (Randall et al., 1976).

In this study, lignocellulosics materials derived from sago bark and leaves will be used to determine their adsorption capacity and their effectiveness in removing dissolved heavy metal
ions from aqueous solutions. According to Quek et al. (1998), Malaysia exports 25,000 to 30,000 tons of sago flour annually and the waste residues from its production are being discharged to rivers. These residues, which are largely composed of lignin and cellulosics (Vikineswary et al., 1994) are, therefore both wastes and pollutants. Like other lignocellulosic materials, sago bark and leaves are also expected to be able to remove heavy metal ions efficiently from wastewater. Even if not as effective as a commercial chelating resin in removing metals from wastewaters, sago bark and leaves can be useful adsorbents in heavy metals removal applications, especially when the low cost and high availability of these materials are considered.

The goal of this research is to develop inexpensive, highly available, effective metal ion adsorbents from natural wastes as alternative to existing commercial adsorbents. The scope of this study will be limited to studying the removal of copper, lead, and nickel ions from aqueous solution. If proven to be effective, these natural waste materials can play an important role in reducing the amount of heavy metals in wastewater.
1.2 Objectives of Study

The general objective of this study is to investigate the adsorption capacities of heavy metal ions from aqueous solutions by lignocellulosics materials derived from sago bark and leaves. Among the specific objectives are:

1. To characterize the lignocellulosics materials derived from sago bark and leaves.
2. To investigate the effectiveness of sago bark and leaves in removing heavy metal ions from aqueous solution.
3. To investigate factors that affect the removal efficiency of heavy metal ions from aqueous solution using sago bark and leaves.
CHAPTER 2: LITERATURE REVIEWS

2.1 Environmental and health effects of the heavy metal

The presence of heavy metal ions in our waters has become a serious problem from the viewpoint of the environmental pollution. Many vital industries such as production of non-ferrous metals, pigments and storage batteries, and metal processing, finishing and plating, discharge heavy metals into their waste streams (Kumar and Dara, 1982).

Copper, lead, cadmium, and mercury are among the heavy metal ions which present as a potential danger in industrial waste waters. According to Randall et al. (1974b), lead and cadmium are perhaps the most dangerous trace elements in our environment, primarily because they are so widespread.

Natural weathering moves 11,000 tons of lead annually to the oceans. Besides, the mining industry also produces four million tons of lead annually (Paasivirta, 1991). According to Hutzinger (1980), in 1970, the effluent of lead from industry to waters is 140,000 and the effluent of lead from car traffic is 300,000 tons per year. Both organic and inorganic lead can accumulate in animal and human tissues to toxic levels. Various effects will occur over a broad range of doses, with the developing fetus and infant being more sensitive than the adult. High levels of exposure may result in toxic biochemical effects in humans which in turn cause problems in the synthesis of hemoglobin, effects on the kidneys, gastrointestinal tract, joints and reproductive system, and acute or chronic damage to the nervous system.
According to Paasivirta (1991), annual production of cadmium is 15,000 to 20,000 tons and it is used in electroplating, in nickel-cadmium batteries, as a polyvinylchloride (PVC) stabilizer, in solders, brazing materials, and other alloys, and in many other technologies. Cadmium is accumulated in the human body, causing erythrocyte destruction, nausea, salivation, diarrhea and muscular cramps, renal degradation, chronic pulmonary problem and skeletal deformity (Mohan and Singh, 2002). Industrial cadmium discharge caused a fatal epidemic of poisonings in the Jintsu River area, Japan in 1947 with 100 deaths until the end of 1965 (Paasivirta, 1991). According to Forstner (1980), the soil contaminated with cadmium is taken up by plants and then enriched in kidneys and livers of the herbivore animals.

Paasivirta (1991) also reported that aluminium, iron, zinc, chromium, and copper are common metallic elements that are strongly bioaccumulating in their salt form. The increased release of these heavy metal ions from the soil due to acid precipitation causes toxic effects to plants and aquatic organisms in lakes. Dissolved aluminium in its various inorganic and organic compounds is both a human neurotoxicant and a serious threat to the plants and also the wildlife (Lewis, 1987). Iron, zinc, chromium, and copper, cause local toxic effects to biota through high concentrations caused by heavy industrial discharges (Paasivirta, 1991). The main source of zinc in wastewater is discharging waste streams from metals, chemicals, pulp and paper manufacturing processes, steel works with galvanizing lines, zinc and brass metal works, zinc and brass plating, viscose rayon yarn and fibre production (Mohan and Singh, 2002).

Besides, low-level exposure of chromium can irritate the skin and cause ulceration, whereas the long-term exposure can cause kidney and liver damage, and damage to circulatory
and nerve tissue. Copper is an essential substance to human life, but in high doses it can cause anemia, liver and kidney damage, and stomach and intestinal irritation (Gardea-Torresdey et al., 1996). Small amounts of nickel are also needed by the human body to produce red blood cells, however, in high doses, can become mildly toxic. Short-term exposure to nickel will not cause any health problems, but long-term exposure can cause decreased body weight, heart and liver damage, and skin irritation. Selenium is another essential substance to humans and other animals in small amounts, but in larger amounts can cause damage to the nervous system, fatigue, and irritability. Long-term exposure can cause hair and fingernail loss, damage to kidney and liver tissue, damage to circulatory tissue, and more severe damage to the nervous system.

Mercury can be found in a variety of oxidation states from elemental mercury(0) to ionic mercury(I) or (II). According to SenGupta (2002), the industrial and municipal sources of mercury(II) include coal-fired plants, geothermal power plants, and incinerator debris from medical research, mining operations, municipal incinerators, and sewage sludge plants. Inorganic mercury poisoning is associated with tremors, gingivitis and/or minor psychological changes, together with spontaneous abortion and congenital malformation. Monomethylmercury causes damage to the brain and the central nervous system, while fetal and postnatal exposure have given rise to abortion, congenital malformation and development changes in young children.

2.2 Overview of lignocellulosic materials

According to Rowell (1995), lignocellulosics referred to as agro-based resources and this include wood, agricultural residues, water plants, grasses, and other plant substances.
Lignocellulosics materials had been evaluated for their effectiveness in filtering toxic heavy metals from stormwater (Han, 1999).

Lignocellulosic are three dimensional, polymeric composites made up primarily of cellulose, hemicellulose, and lignin (Rowell, 1995) and extractives (Han, 1999). Cellulose, a polysaccharide of glucose units, is the most abundant lignocellulosic material and a stable compound. Hemicellulose is a group of heterogeneous polysaccharides (Han, 1999). The combination of cellulose and the hemicellulose are called holocellulose and usually are 65-70 percent of the plant dry weight (Han and Rowell, 1997). Lignins are amorphous, highly complex, mainly aromatic polymers of phenylpropane units and the function in plants is as an encrusting agent in the cellulose/hemicellulose matrix (Han and Rowell, 1997).

According to Han (1999), extractives can be regarded as nonstructural wood or plant constituents and can be identified as fats, phenolics, resin, etc. Except for cellulose, the chemical structure of these components can differ widely. Although all types of lignocellulosic fibres differ in chemical composition, it also have very similar properties, such as, they all swell and shrink as the moisture content of the cell wall changes, they burn, and decay, and they are degraded by acids, bases, and ultraviolet radiation (Rowell, 1995).

The removal of heavy metals can be governed by any of four basic mechanisms: absorption, adsorption, ion exchange, and chelation (Han, 1999). The hemicelluloses are mainly responsible for the moisture sorption. Besides, the accessible cellulose, non-crystalline cellulose, lignin, and surface of crystalline cellulose also play the major roles (Rowell, 1995). According to
Han and Rowell (1997), this is due to the richness of these polymers in hydroxyl groups, which are responsible for moisture sorption through hydrogen bonding. The sorption capacity of lignocellulosic for metal ions is described as adsorption. The cations are attracted to negatively charged active sites throughout the lignocellulosic materials (Han and Rowell, 1997).

However, according to Han (1999), cellulose and lignin make minimum contributions to ion exchange while hemicellulose and extractives play the major roles. This is because the hydroxyl and carbonyl groups are believed to be the main suppliers of active sites and are abundant in lignocellulosics. However, they are tightly bonded to each other in cellulose and lignin and thus are not available unless hydrogen bonding is broken through chemical modification (Han, 1999).

2.3 Sago palms and their uses

Sago palm (*Metroxylon spp*) occurs throughout Malaysia. The main sago area is in Sarawak with an estimated area of 36,437 ha on both peat and mineral soils (Kueh, 1977). According to Johnson (1991), it has several local names: mulong (Iban and Malay), dalo (non-spiny types), balau (spiny types in Kenyah), and balau (bought sago flour in Penan). In Sarawak, sago is grown mostly on peat soils (Tie and Lim, 1976). However, with closer examination of sago areas along Mukah River revealed that most of the sago in this particular locality is being grown on poorly drained mineral soils and shallow peats (Kueh, 1977).
Because of the nature and characteristics of sago with high carbohydrate content, sago possesses high nutritional values and an important source of industrial starch. Sago is not only the main staple food, but also serves other traditional purposes (Sudwikitmono, 1991). For instance, the palm has a variety of local uses; atap, hats, baskets, and blowpipe darts, building roofs and walls are made from the leaves, the sticky sap is used as gum, ripe fruits and palm cabbage are eaten and highly-prized edible sago grubs (larvae of Rhynchophorus schoch) are obtained from the trunks of palms which are about to flower (Johnson, 1991).

Besides, small parts of leaves can be used to make a disposable spoon by folding it a certain way. A very thin length of the leaf can also be used to floss one’s teeth after a meal. A branch can be cut in two equal lengths braided together and fashioned into a very good bag or basket to transport big loads. Cages for chickens or all other types of animals can also be made the same way.

Sago starch is used as a basic ingredient for many food products like biscuits, cookies, veemicelli or ‘sohun’, pudding and others, whereas on the industrial side, sago is used to make alcohol, ethanol, glue, high fructose and maltose syrups as well as chemical and pharmaceutical products. In addition, sago is also widely used in cattle and textile industry (Sudwikitmono, 1991).
2.4 Studies on the removal of heavy metal ions

Various removal methods of heavy metals from waste water have been developed (Wing et al., 1978; Cavaseno, 1980). Among the methods that most commonly used are chemical precipitation, solvent extraction, oxidation, reduction, dialysis/electrodialysis, electrolytic extraction, reverse osmosis, ion-exchange, evaporation, cementation, dilution, adsorption, filtration, flotation, air stripping, steam stripping, flocculation, sedimentation, soil flushing/washing chelation etc (Mohan and Singh, 2002). Each method has its merits and limitations in application.

In the chemical precipitation method, lime (CaO), hydrated lime (Ca(OH)$_2$), caustic soda (50 % NaOH), soda ash (Na$_2$CO$_3$), and sodium sulfide (Na$_2$S) are commonly used as precipitants (Lanouette and Paulson, 1976). This method is the cheapest and most widely used in removing heavy metals from industrial waste water but it does not remove the metals quantitatively (Larsen and Schierup, 1981).

Ion exchange by specific resins is efficient in removing heavy metal ions from solution, especially when the removal of heavy metals by other methods is not successful, or when the recovery of the metals is necessary (Kim and Lim, 1999). However, synthetic ion exchange resins are still expensive (Seki et al., 1997) and with low adsorption capabilities, i.e., the rate and the capacity of adsorption are generally low and small (Morita et al., 1987).
Reverse osmosis is a method used in plating industries to recover or reuse the metals. However, this is basically a process for concentrating ions, and is effective only when the concentration is sufficiently high (Kim and Lim, 1999). Cementation is another process to remove metals, by which metal ions form deposits with more readily, oxidized metals (Manahan, 1990).

According to Adeyiga et al. (1998), the adsorption process with activated carbon has attracted many scientists because of its effectiveness in removing heavy metal ions at trace quantities. Activated carbon can also remove hexavalent chromium, mercury, and various metals complexed with organic materials such as dyes or colorants (Kim and Lim, 1999). However, this method has not been used extensively due to its high cost. Therefore, the uses of low cost materials as sorbent for metal removal from wastewater have been highlighted (Adeyiga et al., 1998).

Larsen and Schierup (1981) investigated the efficiency of barley straw in removing heavy metals from solution. The straw was compared with activated carbon, pine sawdust, and CaCO₃ in the capacity experiments. It was found that 1 g of straw was able to adsorb amounts of zinc, copper, lead, nickel, and cadmium ranging from 4.3 to 15.2 mg, whereas 1 g of activated carbon removed from 6.2 to 19.5 mg, pine sawdust from 1.3 to 5.0 mg and CaCO₃ from 1.6 to 19.8 mg. In column experiments where flow rates of 167 to 370 mL/min were used, the efficiency of the straw was not reduced and this efficiency was improved by 10-90 % when added with CaCO₃.
Wong et al. (2003) studied the modification of rice husk by various carboxylic acids showed that tartaric acid modified rice husk (TARH) had the highest binding capacities for copper and lead. The carboxyl groups on the surface of the modified rice husk were responsible for the sorption of metal ions. The batch experiments showed that the sorption process was pH dependent, rapid and exothermic. The uptake increased with agitation rate. Decrease in sorbent particle size led to an increase in the sorption of metal ions due to an increase in surface area and hence binding sites. Metal uptake was reduced in the presence of competitive cations and chelators. The affinity of TARH for lead is greater than copper.

The use of low-cost activated carbon derived from bagasse, an agricultural waste material, has been investigated by Mohan and Singh (2002) as a replacement for the current expensive methods of removing heavy metals from wastewater. In this study, activated carbon was derived, characterized and utilized for the removal of cadmium and zinc. The uptake of cadmium was found to be slightly greater than that of zinc and the sorption capacity increases with increase in temperature. The kinetics of adsorption depends on the adsorbate concentration and the physical and chemical characteristics of the adsorbent. It was concluded that the adsorption occurs through a film diffusion mechanism at low as well as at higher concentration.

Adeyiga et al. (1998) using tree leaves in the research of the removal of priority metal ions, such as, lead, nickel, zinc from wastewater. The experiments were carried out with 2 g of 40 - 50 mesh leaves in 200 mL synthetic wastewater containing about 50mL/L metal ion and the initial pH of the synthetic wastewater was about 5. The experiments showed that highest removal rate was 96 % for lead, 61.7 % for nickel, and 71.3 % for zinc.
Vazquez et al. (1994) reported that ambient temperature adsorption of metal cations Zn\(^{2+}\), Cu\(^{2+}\) and Pb\(^{2+}\) on *Pinus pinaster* bark pretreated with acidified formaldehyde solution. The influences of the pretreatment conditions and of the pH of the cation solution on the adsorption capacity of the bark were investigated. It was found that the bark was an excellent adsorbent for removal of toxic ions from wastewater with efficiency comparable to commercially available adsorbents, but at a reduced cost. Under favorable conditions, the fractions of dissolved ion adsorbed 85-95\% for Pb\(^{2+}\), 55-85\% for Cu\(^{2+}\) and 51-57\% for Zn\(^{2+}\).

Orhan and Buyukgungor (1993) studied the use of adsorbents such as waste tea, Turkish coffee, exhausted coffee, nut and walnut shells to remove heavy metals from wastewater. Batch studies were conducted at room temperature and adsorption experiments were carried out by shaking 0.3 g of adsorbent with 100 mL synthetic wastewater containing Cr(VI), Cd(II) and Al(III) metal ions. The remaining concentration of heavy metals in each sample after adsorption at various time intervals was determined spectrophotometrically. Batch studies showed that these adsorbents exhibit a good adsorption potential for Al(III) metal ions. The adsorption ratios of Al(III) were as 98, 99, 96, 99.5 and 96\% for waste tea, Turkish coffee, exhausted coffee, nut and walnut shells, respectively.

The abilities of 15 coniferous barks for removing toxic heavy metal ions were investigated by Seki et al. (1977). Of the barks tested, high adsorption ability for heavy metal ions was found in *Picea abies* (Norway spruce). For the equilibrium experiments using *P. jezoensis* (Yezo spruce) bark showed that the adsorption of Cd\(^{2+}\) was greatly affected by the pH of the solution and the initial Cd\(^{2+}\) in solution. The continuous column experiments using
P. jezoensis bark indicated that the packing had retained 10.1-14.2 mg Cd\(^{2+}\)/g adsorbent until the column broke through.

Randall et al. (1974b) reported that a common forest products waste, bark (particularly coastal redwood bark), can be used to selectively remove toxic heavy metal ions from mining and industrial waste waters. The metals are bound to the bark substrates by ion exchange with H\(^+\), presumably from the phenolic groups in tannin compounds. Both batch and continuous column experiments were carried out. Redwood barks bound up to 10 to 20 percent, by weight, of metal ion, which could be stripped by the addition of 0.1 N strong acids, regenerating the substrate for reuse.

Morita et al. (1987) used three chemically modified woods for binding of heavy metal ions. Wood-polyethylenimine composite (wood-PEI) was found to be effective for the adsorption of heavy metal ions such as Hg\(^{2+}\), Cu\(^{2+}\) and other metal ions which tend to form stable ammine complexes. Adsorption of metal ions on a wood-PEI derivative containing dithiocarbamate group (DTC-wood) was higher than that by wood-PEI. The rate of adsorption on these wood-based adsorbents was very high, and adsorption of about 70 percent of total binding capacity was accomplished in the first 1 hour due to a highly porous structure and a hydrophilic nature of the wood which constitutes the skeleton of the adsorbents. Amidoximated wood (AO-wood) prepared by the reaction of cyanoethylated wood with hydroxylamine showed selective adsorptivity for uranium in sea water.
Kumar and Dara (1982) reported that toxic heavy metal cations could be selectively removed from domestic, mining and industrial waste streams using agricultural by-products (bagasse, bark, and onion skin). The metals are sorbed on modified agricultural by-products by ion-exchange or chelation or adsorption. Both equilibrium and column experiments were carried out to determine the rate, selectivity, and capacity of the agricultural substrates for heavy metal cations.

Meunier et al. (2003) studied the efficiency of cocoa shells to remove heavy metals from acidic solutions (pH 2) and investigate how the composition of these solutions influences heavy metal uptake efficiency. Adsorption tests were conducted in agitated flasks with single-metal solutions, multi-metal and an effluent obtained from chemical leaching of metal-contaminated soil, in the presence of different cocoa shell concentrations (5–40 g/L). Cocoa shells are particularly efficient in the removal of lead from very acidic solutions. The presence of other metals and cations in solution did not seem to affect the recovery of lead. This research had also demonstrated that the removal of metals caused a decline in solution proton concentration (pH increase) and release of calcium, magnesium, potassium and sodium from the cocoa shells.