Adsorption of Zinc and Copper Ions Using *Pinus sylvestris*

by

Syakirah binti Mohamed

Dissertation submitted in partial fulfillment of
the requirements for the
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(Civil Engineering)

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CERTIFICATION OF APPROVAL

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Approved by,

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

Syakirah

SYAKIRAH BINTI MOHAMED

ABSTRACT

Fixation of heavy metals (Zn(II) and Cu(II)) onto pine cone fruits or *Pinus Sylvestris* is presented in this report. Batch experiment was conducted to study the main parameters such as adsorbent concentration, initial adsorbate concentration, contact time and co-existence with other metal ions in a solution on the sorption of Zn(II) and Cu(II) by pine cone fruits. The equilibrium of a solution between liquid and solid phases is described by Langmuir model. The capacity of the Zinc ions to bind onto the biomass was 11.75 mg/g for C_o = 100 mg/L and 0.78 for C_o = 10 mg/L. the maximum adsorption capacity for copper in copper only and copper-zinc solution was 1.7 and 1.5 mg Cu(II) / g, respectively. From these results, it can be concluded that the pine cone fruits of *Pinus Sylvestris* could be a good adsorbent for the metal ions coming from aqueous solutions. Moreover, this material could also be used for purification of water before rejection into the natural environment.

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May Allah bless you all and may all your days filled with joy and happiness.

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CHAPTER 1

INTRODUCTION

1.1 Background Study

In many countries, the wastes from industrial processes are being produced in ever increasing amounts and may contain toxic and poorly degradable compounds. They are often considerably stronger than domestic sewage, which many treatment systems are only designed to handle. In addition, the consumption of water from domestic and industrial use has increased to such a degree that nowadays it is not unusual to find that the rivers receiving treated effluents cannot give the dilution necessary for their survival as good quality watercourses, a problem aggravated during periods of drought [11]

The presence of heavy metals in the environment can be detrimental to a variety of living species including human. Metals can be distinguished from other toxic pollutants, since they are non-biodegradable and can accumulate in living tissues, thus becoming concentrated throughout the food chain. Many researchers have made efforts to remove these heavy metals from industrial wastewater using several processing method such as chemical precipitation, evaporation, ion exchange, cementation electrolysis and reverse osmosis. However these conventional technologies appear to be inadequate and expensive. They often create secondary problems with metal-bearing sludge.[15]

Because activated carbon has a strong affinity for binding organic substances, even at low concentrations, it has become the premier method for treating organic-laden wastewaters. It also is widely used for purifying drinking water from sources containing relatively small but offensive levels of organic contaminants.[11]

Formaldehyde used in the activation stage is a colorless, strong-smelling gas. It is one of the large families of chemical compounds called volatile organic compounds or "VOCs", which means that it vaporize at normal room temperatures. It is widely used to manufacture building materials and numerous household products. There are two types of formaldehyde resins: urea formaldehyde (UF) and phenol formaldehyde (PF). Formaldehyde is an important industrial chemical used to make other chemicals, building materials, and household products.[17]

Sulphuric acid is a colourless viscous corrosive oily liquid. It is an important industrial chemical and it has many uses as a strong oxidising agent and a powerful protonating agent. Sulphuric acid is also a powerful dehydrating agent and is used to remove a molecule of water from many organic compounds. Commercially available sulphuric acid is as a 96-98% solution of the acid in water.[18]

Zinc is the 23rd most abundant element in the earth's crust. Zinc uses range from metal products to rubber and medicines. About three-fourths of zinc used is consumed as metal, mainly as a coating to protect iron and steel from corrosion (galvanized metal) and as alloying metal to make bronze and brass. The remaining one-fourth is consumed as zinc compounds mainly by the rubber, chemical, paint, and agricultural industries. Zinc is also a necessary element for proper growth and development of humans, animals, and plants; it is the second most common trace metal, after iron, naturally found in the human body.[19]

Copper is usually found in nature in association with sulfur. Copper is one of the oldest metals ever used and has been one of the important materials in the development of civilization. Because of its properties, singularly or in combination, copper has become a major industrial metal, ranking third after iron and aluminum in terms of quantities consumed. Electrical uses of copper account for about three quarters of total copper use. Copper byproducts from manufacturing and obsolete copper products are readily recycled and contribute significantly to copper supply.[20]

The pine cone fruits *(Pinus Sylvestris)* used in the research was collected at Village 1 Residential College. The trees are thought to represent polyphyletic colonization and adaptations to harsh environments across a very broad front. Trees from the extreme west of the range show resin chemistry and adaptations to oceanic climates not found in the rest of the species' range. These trees are thought to have survived the ice ages; as yet there has been no research as to whether this small endangered population deserves taxonomic recognition. The tree is 25-40 m tall. The cones are 3-6 cm long, conic, symmetrical or nearly so, green ripening matt grey-buff to grey-green.; mature, open and fall soon after seed shed.[21]

Figure 1: Pine cone fruits

1.2 Problem Statement

The presence of heavy metals in streams and lakes has been responsible for several health problems with animals, plants, and human beings. Numerous metals such as Sb, Cr, Cd, Pb, Mn, Hg, etc. have toxic effects on man and his environment. The consumption of food containing traces of these elements may lead to various diseases, for example, the consumption of (i) rice containing high concentrations of cadmium (0.37 at 3.6 mg l−1) led to a surge in the Ita¨ı-Ita¨ı disease in Japan in 1955 [1,2], and (ii) fish contaminated with methylmercury led to Minamata disease.[15]

For these reasons, the legislation is progressively becoming more stringent; for example, the maximum concentrations of metals in drinking water according to Environmental Quality (Scheduled Wastes) Regulation 1989 are now: 0.01 mg l−1 for Pb(II) and 0.02 mg l−1 for Cd(II).[5] However, these values are higher due to accumulation phenomena observed when the spreading operations are used instead of direct overflowing into rivers. The enforcement of the law had affected industries related to metal, especially the small and medium scale where the expertise in wastewater treatment is unavailable.

Precipitation methods to remove heavy metals in aqueous solutions are particularly reliable but require large settling tanks for the precipitation of voluminous alkaline sludge and a subsequent treatment is needed.[2] Ion-exchange has the advantage of allowing the recovery of metallic ions, but it is expensive and sophisticated. This has encouraged research into discovering materials that are both efficient and cheap. The by-products and wastes from the agricultural and forest industries were studied as these materials could be assumed as low-cost since they require little processing and are abundant in nature. [1]

The idea of using low cost carbons and agricultural products and by-products for the removal of toxic metals from waste water has been investigated by a number of authors. Studies to assess the ability of scrub rubber to adsorb dissolved metal ions from waste water found it to be a moderately effective adsorbent.[1]

1.3 Objective and Scope of Study

The objective of this preliminary study was to investigate the feasibility of metallic ions removal from aqueous solution by fruits of *Pinus Slyvestris*

The scope of this research was narrowed to investigate Zn and Copper ions adsorption by pine cone fruits. The effects of various factors on the removal were determined. The factors investigated included:

(i) Adsorbent concentration of activated carbon
(ii) Contact time between adsorbent and adsorbate
(iii) Raw and treated (activated) adsorbent
(iv) Single component and multi-component metal sorption
(v) Best adsorption isotherms for the Zn ion

CHAPTER 2

LITERATURE REVIEW

2.1 Removal of Heavy Metals

In recent years public awareness has increased as to the long term toxic effects of water containing dissolved metal ions. Numerous industrial processes produce aqueous effluents containing heavy metals contaminants. These pollutant concentrations must be reduced, to meet ever increasing legislative standards, and recovered where feasible. According to World Health Organization, the metals most immediate concern are aluminum, chromium, manganese, iron, cobalt, nickel, copper, zinc, cadmium, mercury and lead.[5]

Consequently, improved and innovative methods of waste water treatment are continuously being developed to deal with waste metals not readily compatible with or economically feasible to, removal by traditional methods.

The vast majority of toxic metal pollutants are waste products of industrial and metallurgical processes. In particular the effluents from electroplating plants, extractive metallurgy processes and metal treatment/finishing operations contain particularly high concentrations of dissolved metals.

The most common methods of removal of metals from industrial effluents include chemical precipitation, solvent extraction, electro dialysis, cementation, reverse osmosis, evaporative methods, ion-exchange resins, carbon adsorption and dilution. In recent years carbon adsorbents have become the accepted medium for the physiochemical treatment of waste water generally, while the most common metal processes have been chemical precipitation and electrolytic methods.[2]

Adsorption processes are widely used to remove pollutants from waste waters and waste gases. More recently, awareness and concern has increased as to the long term toxic effects of water containing dissolved metal ions and organic compounds, and of air containing nitrate compounds. The concentrations of these undesirable constituents must be reduced to meet ever increasing legislative standards. The importance of activated carbon as an adsorbent material is not under question here, however, a wide range of carbons exist as possible use as adsorbents and it is becoming necessary to select carbons or even other adsorbent materials which are the most suitable adsorbents for the required duty. A carbon which is effective at removing dye from a wastewater may not be as effective at removing metal ions or phenols from the water and nitrate compounds from air. [2]

2.2 The Nature of Adsorption

Adsorption is a separation process where one or more components of a gas or liquid stream are adsorbed on the surface of a solid adsorbent. Adsorbent refers to small particles which adsorb the material to be recovered (adsorbate). One of the most common adsorption applications in liquid phase is the removal of organic compounds and impurities from water in water treatment. The adsorbents are physically in the form of small pellets, beads, and granules (0.1mm to 12 mm). The structure of the adsorbents are porous, which are divided into macro pore (>500 A), meso pore (20 – 500 A) and micro pore (<20A). It has specific surface area ranged from 300 to 1200 m^2/g.[3]

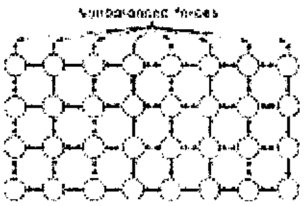

Figure 2: Representation of forces in a solid

Adsorption process occurs when solute (adsorbate) diffuses from bulk fluid to exterior surface of adsorbent. The solute is then diffuses inside the pore where finally it will be absorbed on the surface of the pore. The adsorbate is attached to the adsorbent by two means, namely physical adsorption (van der Waals attraction) and chemisorptions (by activated adsorption). Physical adsorption occurs when intermolecular attractive forces between molecules of a solid (adsorbent) and adsorbate are greater than those between molecules (adsorbate) itself. For the chemisorptions, separation occurs due to formation of chemical bonds between adsorbate and adsorbent. [4]

Criteria for a good adsorbent are: [3]

(i) High selectivity to enable sharp separations.
(ii) High capacity to minimize the amount adsorbent needed.
(iii) Favorable kinetic and transport properties for rapid sorption.
(iv) Chemical and thermal stability to preserve the amount and its properties.
(v) Hardness and mechanical strength
(vi) High fouling resistance
(vii) Capability of being regenerated at relatively low cost.

Activated carbons, both powdered and granular, are made from a wide variety of carbonaceous starting materials: coals, wood, peat, coconut shell, etc. they are manufactured in such a way that they have tremendous network of pores inside. It is in this extensive surface on which adsorption of organics can occur.

2.3 Factors Affecting Physical Adsorption

Various factors affect the extent to which a given compound will adsorb to activated carbon.[6]

i. Activation Effect

The structure of the carbon materials is much influenced by the activation process. In this step, the activating agent erodes the internal surfaces of the carbon thus develops an extensive and fine network of pores in the carbon. This oxidation process changes the surface atoms to specific chemical forms which have selective adsorption capabilities. The digestion of pine cone fruits with sulphuric acid will produce gaseous species that creates pores in the carbon (pine cone fruits). The total time period of the carbon digested in sulphuric acid is called the activation time. This activation time is a vital variable to determine the activated carbon properties.

Longer activation time will permit the acid to create more pores in the carbon; hence will increase its internal surface area. However if the activation time is too long, the pores created are too large or too much and will make the support of the activated carbon to be unstable. When this happened, the activated carbon structures will disintegrate and break. Thus the activated carbon will have less mechanical strength to withstand the adsorption process. In addition, as the size of the pores increases to a certain extent which is too large, the total internal surface area of the activated carbon will decrease. The larger pores also could affect the adsorption process where the undesired material could be adsorbed along.

Figure 3 shows an activated carbon purposely prepared so as to induce a very high degree of transition pore porosity for increasing the diffusion-limited rate of adsorption from solution. Area shown is 15.8 x 12.5 μm. A granule of a less porous carbon is shown in Figure 4 for comparison. Area shown is 30 x 27 μm. It is important to point out that the physical parameters such as porosity can be controlled to some degree to produce carbons suited for special applications.

Figure 3: Scanning electron photomicrograph of an activated carbon surface.

Figure 4: Scanning electron photomicrograph of a relatively “non macroporous” carbon.

ii. Solute Nature

The polarity of the solute has intense effect of its adsorptive capability. In certain highly dissociated solutes such as sodium chloride and potassium chloride, the tendency to be adsorbed are less compared to non dissociating solutes like iodine and mercury chloride which are well adsorbed. Most of the carbon surface exhibits hydrophobic characteristics that is non polar. The hydrophobic reactions originate from the net repulsion between the water and non-polar region of the carbon surface as well as the non-polar moieties of the solute. As a consequence of these repulsive interactions and high cohesive energy of water, the non-polar molecules and non-polar regions of the surface can associate when they are close proximity to each other.

So it can be concluded that in aqueous systems, non-polar solutes are more strongly adsorbed than polar solutes.[14]

iii. Pore Structure of the Adsorbent

Pore structures of an activated carbon plays important role to determine the adsorbent molecules selectivity. These pore structures which has various size from 10 to 100,000Å control the sizes of molecules accessible to them.[12]

iv. Surface Chemistry

Specific functional groups on the adsorbent surface which have certain characteristics affect the adsorption process. The formation of polar surface group of chemisorbed oxygen during the activation process of activated carbon affects the adsorptive capacity for many solutes. Surface oxides consisting of acidic functional groups reduce the capacity of carbon adsorption of many organic solutes. This was attributed to the preferential adsorption of water and hence blockage of a part of the surface. The abundance of surface oxides consisting of carbonyl group enhances the adsorption of such aromatics solutes as phenol and naphthalene.[12]

v. Temperature

Higher environment temperature will decrease the adsorption rate. It is because higher temperature wills generates greater vibration energy to the adsorbed molecules and will make it more likely to desorb from the surface. Regarding this matter, it is recommended to place the sample in ambient temperature under isothermal condition during the adsorption steps.[13]

vi. Surface Area of Adsorbent

Generally, the larger the surface area of the activated carbon, the higher adsorption capacity it has. Proper steps should be taken during the activation steps to ensure that the internal surface area of the carbon is activated adequately.[12]

vii. pH of the solution

It is well known that substances adsorb poorly when they are ionized. When the pH is such that an adsorbable compound exists in ionized form, adjacent molecules of the adsorbed species on the carbon surface will repel each other to a significant degree, because they carry the same electrical charge. Thus, the adsorbing species cannot pack together very densely on the surface.[16]

In contrast, when the adsorbing species is not ionized, no such electrical repulsion exists, thus the packing density on the surface can be much higher. This explains the common observation that no ionized forms of acidic and basic compounds adsorb much better than their ionized counterparts. Acidic species thus adsorb better at low pH, and basic species adsorb better at high pH.

2.4 Preparing Activated Carbon from Pine Cone Fruits

Activated carbon is produced from carbon-rich raw materials. Currently, activated carbon is manufactured from wood, coal, coconut shell and peat. Generally, any organic materials which have large percentage of carbon are capable to be activated, hence will increase the material's sorptive characteristics.[7] However in order to get a good activated carbon, several material characteristics are taken into accounts which are:

- High adsorptive capability
- The ability to maintain its properties under usage condition
- Have long storage life

Mainly the two steps to prepare the activated carbon are activation and carbonization. Even though all carbon based material is able to be transformed to be activated carbon, the final product of the activated carbon will be different depending on the parameters set during the preparation steps. The nature of the raw material used and the agent raw material also play important role on affecting the final characteristics of the activated carbon prepared.

i. Activation Step

The activation of a carbon material increases the volume and enlarges the diameters of the pores of the carbon. Initially the aromatic sheets of the carbon exposed to the action of activation agents which will leads to the development of microporous structure. Further on, the latter effect is the widening of the existing pores in the carbon and the formation of large sized pores by the complete burnout of the walls between the adjacent pores. This effect initiate the increment of the transitional pores and the macroporosity, where else decreases the volume of the micropores.[14]

The intermediate carbonized products which are formed by activation have carbon atoms that differ from each other in its reactivity based on their spatial arrangement. The carbon atoms which are located at the edges and periphery of the aromatic sheets or those located at defect positions and dislocations or discontinuities are associated with unpaired electrons or have residual valencies which are rich in potential energy. As a result, these carbon atoms are more reactive and have a tendency to form surface compounds by oxidation. Later these will break down and peel off the oxidized carbon from the surface as gaseous oxides leaving behind new unsaturated carbon atoms for further reaction with the activating agent.[8]

ii. Carbonization Step

In the carbonization step, most of the non-carbon elements in the activated carbon like oxygen and hydrogen are eliminated as volatile gaseous products. The residual carbon atoms group themselves into sheets of condensed aromatic ring systems with a certain degree of planar structure. The irregularity of the mutual arrangement of the aromatics sheets leaves free interstices between the aromatic sheets which may be filled with the tarry matter or the products of decomposition or at least blocked partially by the disorganized carbon. These interstices increase the pores total, which make activated carbons excellent adsorbents.[14]

2.5 Adsorption Isotherms

Equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms (Langmuir, Freundlich, and BET). Adsorption equilibrium is established when the concentration of contaminant remaining in solution is in dynamic balance with that at the surface of the solid. It is much affected with the pH, temperature, and other parameters upon the adsorption process.[11]

i. Langmuir Isotherm

In the development of the Langmuir isotherm, it is assumed that the solute is adsorbed as a monomolecular layer at the surface of the adsorbent. Langmuir isotherm is developed based on four important assumptions as follows:

(i) Adsorption occurs at definite localized sites on the surface
(ii) Each site can bind only one molecule of the solute
(iii) The energy of adsorption (strength of the bond) is the same for all sites
(iv) There are no forces of interaction between adjacently adsorbed molecules

This is the most often used adsorption isotherm, being given by the relationship

$$X/M = KbC_e / (1+KC_e)$$

Where;

X = weight of solute adsorbed (adsorbate, mg)

M = weight of adsorbent (g)

K = the equilibrium constant (cm3 of adsorbent/mg of adsorbate)

C_e = the equilibrium concentration of solute (mg/liter)

b = a constant which represents the monolayer coverage per unit weight of adsorbent (mg of adsorbate / g of adsorbent).

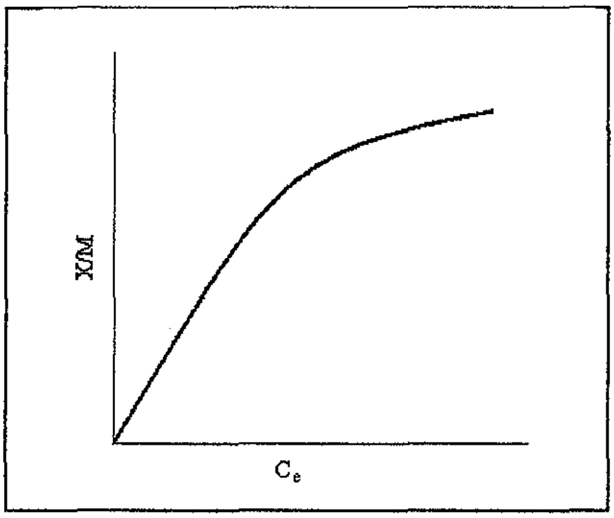

Figure 5: Langmuir isotherm

The equation can be rewritten in linear form by taking the reciprocal of both members:

$$1/(X/M) = (1/Kb)\ (1/C_e) + (1/b)$$

A plot of $1/(X/M)$ versus $1/C_e$ yields a straight line, which permits determination of parameters K and b from its slope and ordinate intercept, respectively.[11]

ii. Freundlich Isotherm

Freundlich Isotherm is the most widely used mathematical expression of adsorption in aqueous systems. The Freundlich isotherm is expressed by the equation

$$X/M = kC_e^{1/n}$$

X/M and C_e have the same meaning as in Langmuir's isotherm, and k and n are constants dependent on several environmental factors. In linear form, the equation is re-written by taking logarithm of both members:

$$\log (X/M) = (1/n) \log C_e + \log k$$

a logarithmic plot of X/M versus C_e yields a straight line, which permits determination of parameters n and k from its slope and ordinate intercept at $C_e = 1$.[11]

CHAPTER 3

METHODOLOGY

3.1 Sample Preparation

These are the steps to produce activated carbon from pine fruit in sequence:

The sample (pine fruit) was first washed with distilled water to remove all the contaminants such as dust, small insects etc. Although it was quite impossible to remove all the contaminants from the sample, by minimizing it the purity of the composition could be preserved.

After cleaning, the sample was put on a tray for the drying process. The importance of the drying phase was to remove all the volatile components and moisture content exist in the pine cone fruits. The drying was carried out in oven for 24 hours with 110 °C temperature to ensure all the volatile components were successfully removed.

Grinding was carried out using Panasonic Blender and Mill. The grinder machine was first set at the minimum speed which will result in coarse size of pine fruit. The speed is then gradually increased to get finer size of sample powder. It was important to set the grinding size range and timing appropriately to prevent sample to become too fine or worse become dust.

Sizes of the sieve chosen for characterization process were 112 μm and retained on pan. The sieving time was set at 10 minutes and the weight retained on each tray was taken, so that the total weight was to be more than 400 grams.

Acid dilution step was to prepare the acids for the activating process. 20% formaldehyde was mixed with 0.2N H_2SO_4 to get the proportion of 1:4 volume-to-volumes.[8]

Sample retained on tray size 75 μm was added to the activation mixture prepared at earlier stage, to give the proportion of sample to formaldehyde 1 gram to 10 mL. The mixture was then stirred for 2 hour at 50^0C. The mixture was then cooled to room temperature and filtered.[9]

The digested pine fruits were then filtered off and washed with excess distilled water to neutralize the pH until the pH of the washing was 6. The vitality of this step was to stop the acid digestion at the respective time that was been located earlier. The pH was checked by using the pH meter.

After being washed, the sample was air dried for 18 hours. This was to remove the moisture content before the samples were taken to be analyzed. In the case of industrial waste, it was shown that this treatment was not necessary.[10]

3.2 Sample Analysis

After the sample was prepared, analysis steps on the sample were conducted which were:

i. Preparation of Standard Solution

The concentrations of the standard solution were prepared to be within the range 1 to100 ppm. These standard solutions were very important since the standard solution curve obtained from the Atomic Adsorption Spectroscopy is very crucial.

ii. Adsorption Step

a. The first analysis was carried out by shaking 0.2 g of treated sample for every 250 mL with initial zinc concentration 5 mg/L in volumetric flask. The pH of the solutions was varied at pH 3, 4, 6, 7, 9 and 10 by adding either sulphuric acids or sodium hydroxide.[25] The samples from 3 bottles for each pH (total 18 bottles) were shaked for 6 hours and filtered.

b. 100 mL zinc with initial concentration of 10 mg/L in 15 volumetric flasks were added with 3 sets of sample weighed 0.4, 0.6, 0.8, 1.0 and 1.4 grams. The mixtures were shaked for 1, 2, 3, 4, 6 and 24 hours and filtered. The same steps were carried out with initial concentration of 100 mg/L.

c. 3 sets of raw and treated samples of 0.4, 0.6, 0.8, 1.0 and 1.4 grams were added to 15 volumetric flasks containing 100 mL zinc solutions with initial concentration of 10 mg/L. The samples were shaked for 24 hours and filtered. The same steps were carried out with copper solutions of initial concentration 10 mg/L and mixture of 10 mg/L of copper with 10 mg/L of zinc.

Figure 6: Sample added into ion solution

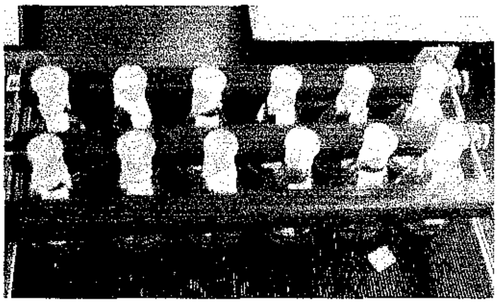

Figure 7: Mixture of sample and ion solutions were shaked for 2 to 24 hours

Figure 8: After designated contact time, mixtures were filtered using filter paper

iii. Adsorption Analysis

Concentration of unadsorbed Zinc and Copper ions in the effluent were determined using Shimadzu AA-6800 atomic Absorption Spectrophotometer equipped with a Zeeman atomizer and a SSC-300 auto sampler. All experiments were carried out at room temperature.

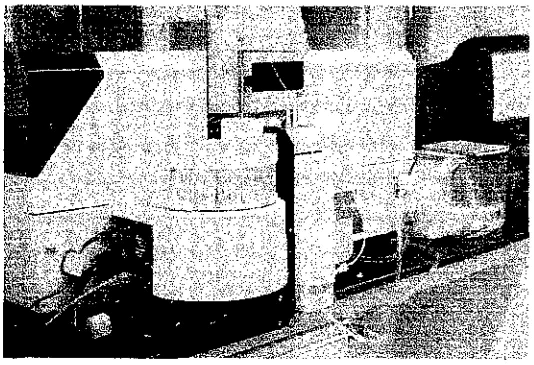

Figure 9: Effluent was analyzed using Shimadzu AA-6800

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Effect of time variance on Zinc sorption

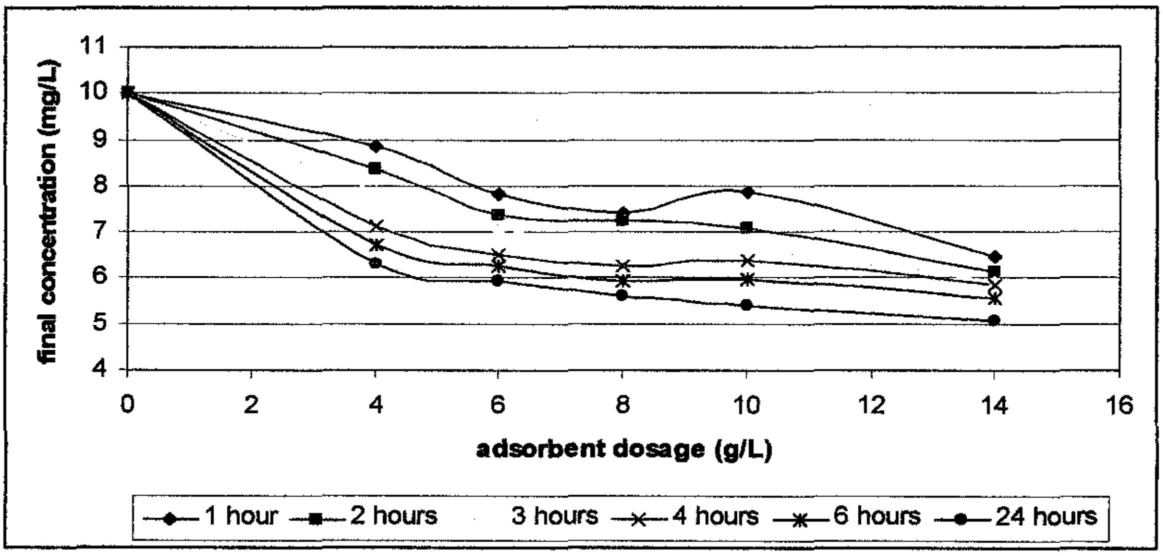

Figure 10: Final concentration of Zinc against adsorbent dosage for $C_0 = 10$ mg/L at varied time

Figure 10 shows final concentration of zinc against adsorbent dosage for zinc initial concentration of 10 mg/L by varying the contact time at 1, 2, 3, 4, 6 and 24 hours. The experiment was carried out using treated sample.

The graph shows that for the same contact hour, the higher the adsorbent dosage, the lower final concentration becomes. For the same amount of adsorbent dosage, longer contact time resulted in lower final concentration compared with shorter duration.

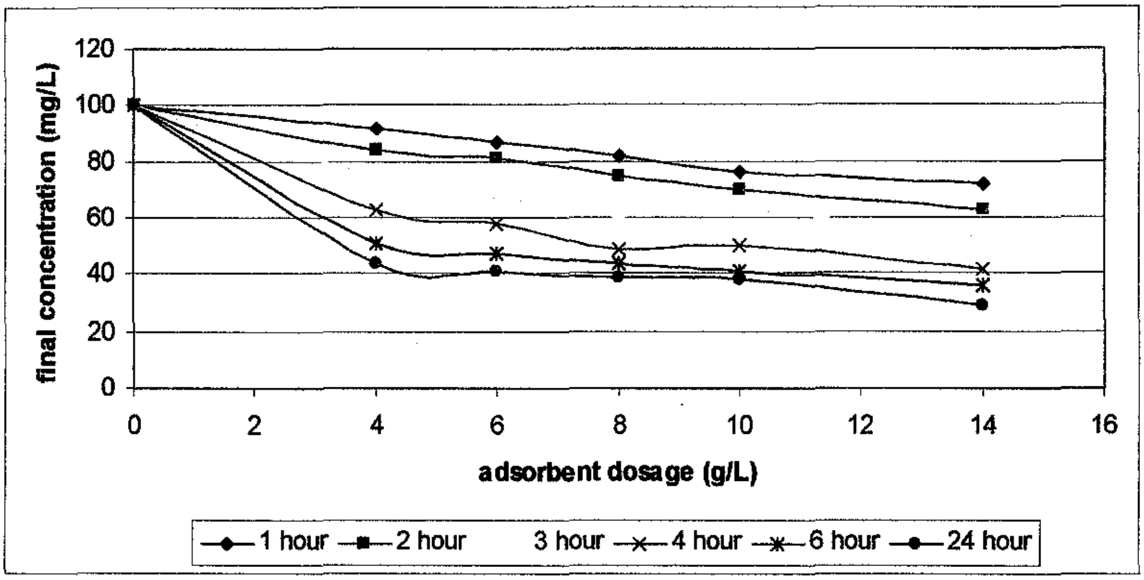

Figure 11: Final concentration of zinc against adsorbent dosage for C_0 = 100 mg/L at varied time

Figure 11 shows final concentration of zinc against adsorbent dosage for zinc initial concentration of 100 mg/L by varying the contact time at 1, 2, 3, 4, 6 and 24 hours. The experiment was also carried out using treated sample.

The graph shows the same trend as the previous experiment. Generally, the higher the adsorbent dosage, the lower final concentration becomes. When using the same amount of adsorbent dosage, longer contact time resulted in lower final concentration compared with shorter duration.

The maximum Zinc removal for both 100 mg/L and 10 mg/L initial concentration achieved are 71% and 49% respectively, by exposing 14 g/L of treated pine cone fruit for 24 hours.

4.2 Effect of adsorbent dosage variance on Zinc sorption

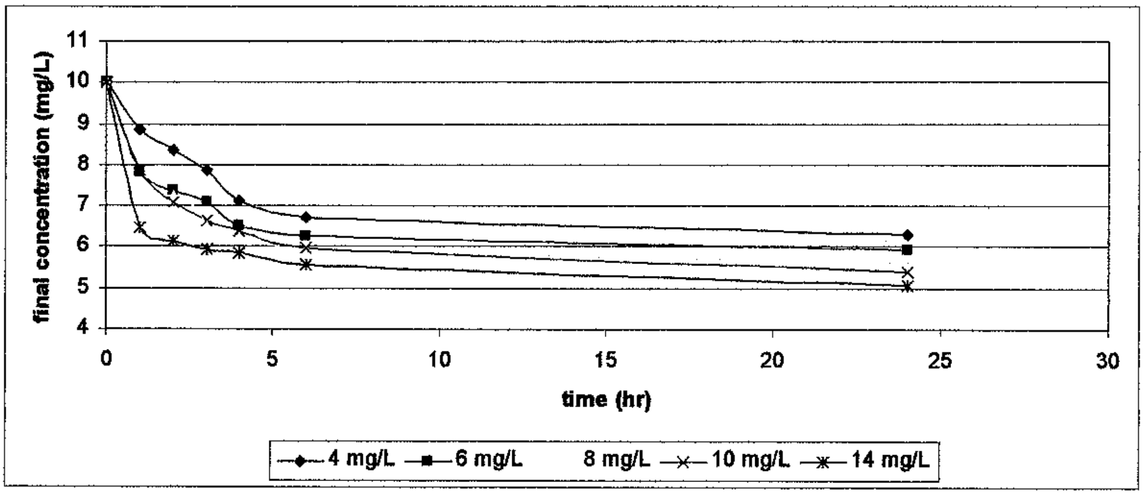

Figure 12: Final concentration of zinc against time for $C_0 = 10$ mg/L at varied adsorbent dosage

Figure 12 shows final concentration of zinc against time 1, 2, 3, 4, 6 and 24 hours at varied adsorbent dosage. The adsorbent used were treated pine cone fruits, in amount of 4, 6, 8, 10 and 14 g/L.

The trend shows that longer contact time resulted in lower final concentration. For the same period of contact time, larger dosage removed more zinc compared to less adsorbent used.

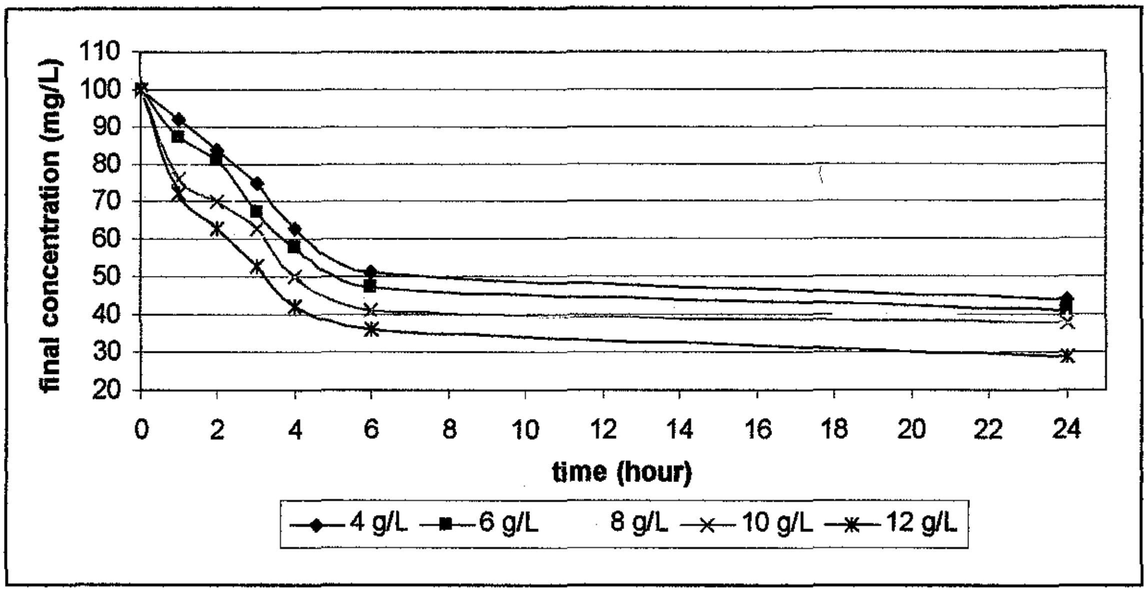

Figure 13: Final concentration of zinc against time for $C_0 = 100$ mg/L at varied adsorbent dosage

Figure 13 shows final concentration of zinc with 100 mg/L initial concentration against time from 1 to 24 hours at varied adsorbent dosage of 4, 6, 8, 10 and 12 g/L, using treated sample.

The graph shows the same trend as the previous experiment. Generally, the longer the contact time, the lower final concentration becomes. When exposed to the same contact time, larger adsorbent dosage resulted in lower final concentration compared with smaller dosage.

The maximum Zinc removal for both 100 mg/L and 10 mg/L initial concentration achieved were 71% and 54% respectively, by exposing 14 g/L of treated pine cone fruit for 24 hours.

4.3 Effect of adsorbent dosage & contact time for zinc uptake capacity

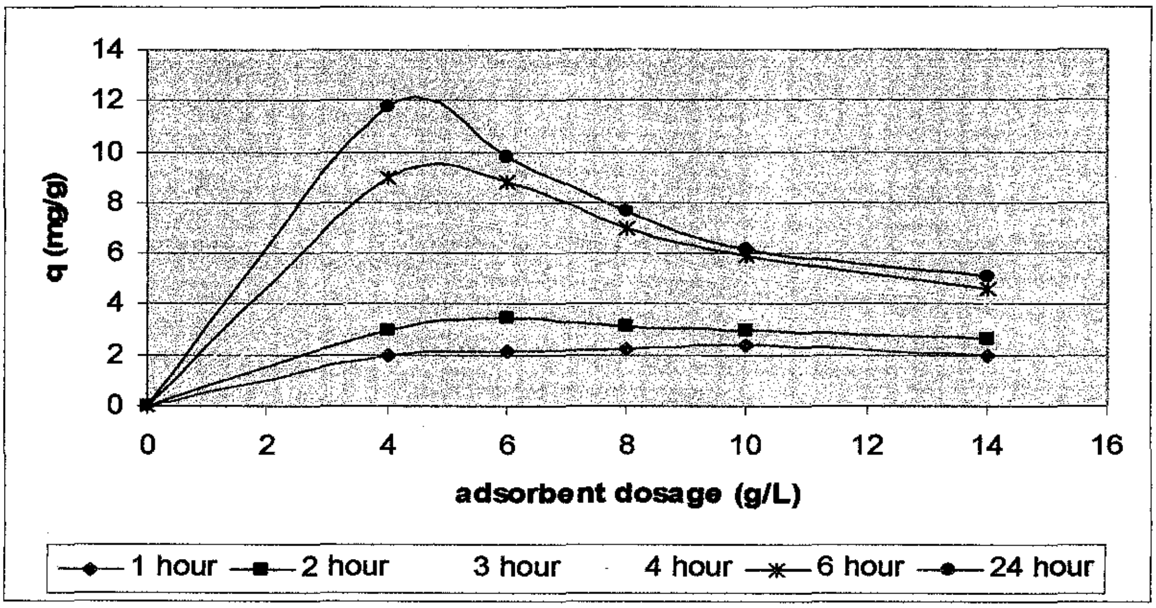

Figure 14: Influence of adsorbent dosage and contact time on the sorption capacity of zinc at $C_o = 100$ mg/L

In order to evaluate the effect of amount of adsorbent, the adsorption experiment was done on the pine fruits that were activated at pH 4. Initial zinc concentration was 100mg/L and contact time varied from 2 to 24 hours. The weight of the sample was varied at 0.4, 0.6, 0.8, 1.0 and 1.4 grams for every 100mL of zinc solution. These results were plotted in Figure 14 above.

The figure shows that the maximum zinc ions uptake was 11.75 mg of Zn(II) / g of pine cone fruits at 24 hours contact time. The optimum dosage of adsorbent was 4 gram for every 1 L of adsorbent. The figure also shows that the longer the contact time, the higher was the Zinc uptake.

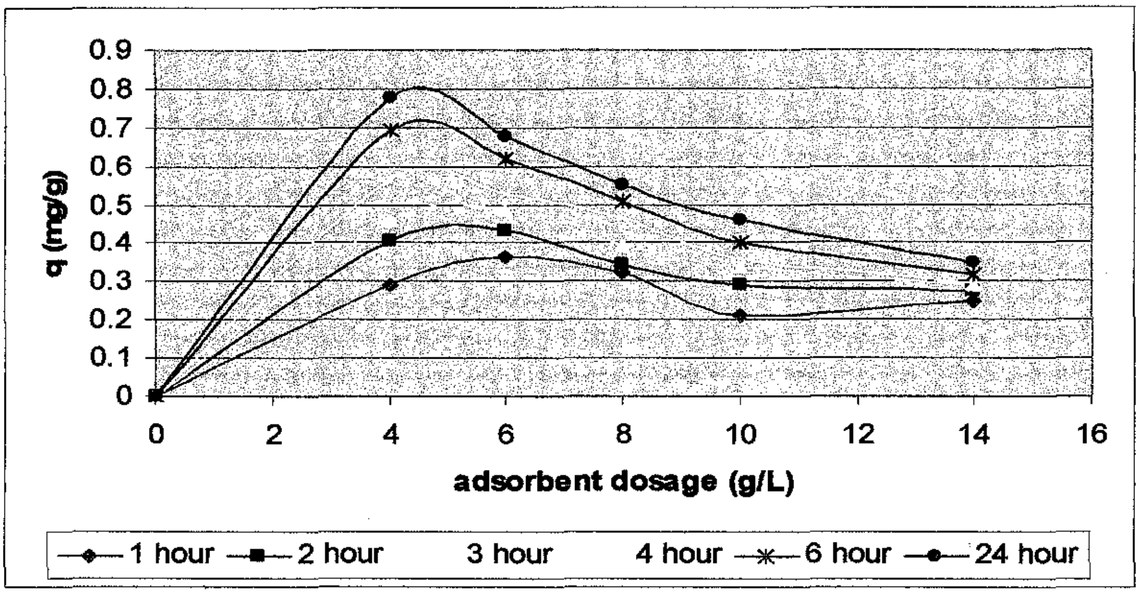

Figure 15: Influence of adsorbent dosage and contact time on the sorption capacity of zinc at $C_o = 10$ mg/L

In order to evaluate the effect of amount of adsorbent for initial concentration of zinc 10 mg/L, the adsorption experiment was done on the pine fruits that were activated at pH 4. Contact time varied from 2 to 24 hours. The weights of the sample were varied at 0.4, 0.6, 0.8, 1.0 and 1.4 grams for every 100mL of zinc solution. These results were plotted in Figure 15 above.

From the results, it can be observed that the maximum zinc ions uptake was 0.78 mg of Zn(II) / g of pine cone fruits at 24 hours contact time. The optimum condition of zinc removal was when the adsorbent dosage was 14 mg/L. It indicates that the longer the contact time, the higher was the Zinc uptake.

Comparing results from both Figure 14 and 15, after 24 hours, when the initial metal ions concentration was increased from 10 to 100 mg/L, the loading capacity of pine cone fruits increased from 0.78 to 11.75 mg of Zn per gram of pine cone fruits. Ion removal is highly concentration-dependent. This increase in loading capacity of the sorbent with relation to metal ions concentration is probably due to a high driving force for mass transfer. In fact, the more concentrated the solution is, the better the adsorption is.[10]

4.4 Effect of pre-treatment on Copper sorption

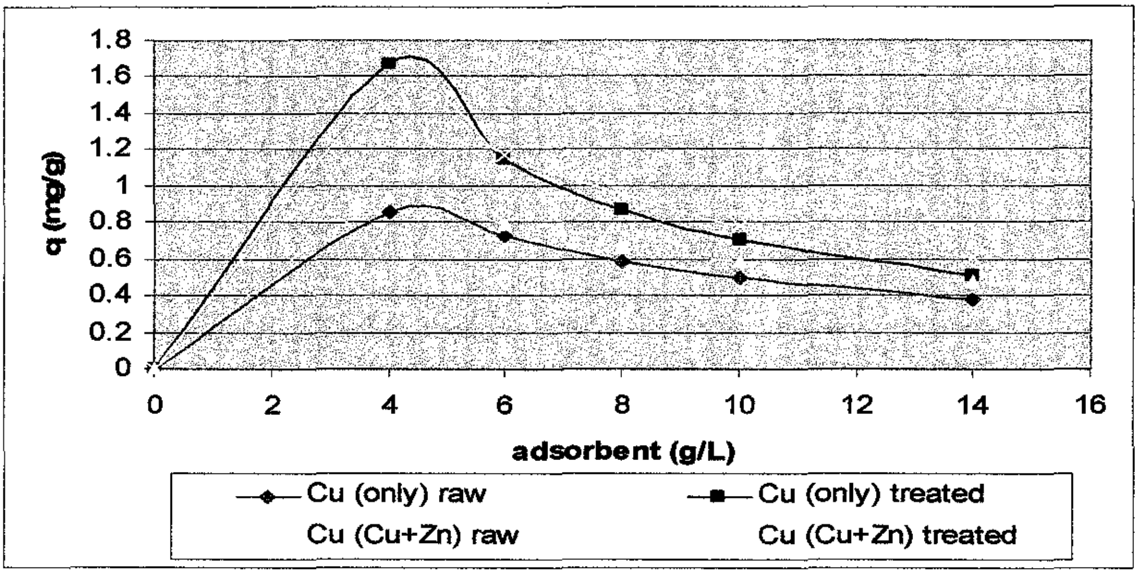

Figure 16: Influence of pretreatment and binary system on the sorption capacity of copper at C_o of zinc and copper = 10 mg/L (contact time = 24 hr)

The effect of pre-treatment on the sorption was examined by using the experimental procedure previously described. The solution with initial concentration of 10 mg/L was stirred with 4 to 14 g/L of treated pine cone fruits. Another experiment was carried out with untreated pine cone fruits. Figure 16 shows the retention capacities of treated and untreated pine cone fruits for copper ions sorption after a contact time of 24 hours.

The result shows that cone fruits activated with sulphuric acids and formaldehyde has higher copper ions intake. From the result, it can be observed that the highest copper ions intake was 1.7 mg Cu(II) / g of activated carbon compared to the untreated adsorbent which yield 0.86 mg Cu(II) / g of adsorbent.

It indicates that activation provides higher microporosity of the adsorbents as activation agent increased the surface area and micropores volume.[11] At first thought, the amount of substance which a carbon can adsorb would seem to be directly proportional to the internal surface area. Yet, such is not always true. One must be aware that the surface area is usually inferred from the amount of small molecule which can be adsorbed. If one wish to adsorb a large molecule, much of the internal surface area may not be accessible.[13] The pore structure is important because pore diameters control which sizes of molecules are accessible to them.[11]

4.5 Effect of multi-component metal ions system

To study the effect of multi-component ions system on the adsorption of copper, an experiment was carried out on pine cone fruits that were both raw and activated by sulphuric acids and formaldehyde. Biosorbent particles (0.4 – 1.4 g) were left in contact with 100 mL of solution which comprised of mixture of 10 mg/L of zinc and 10 mg/L of copper solutions during 24 hours.

Figure 16 again shows that co-existence of zinc and copper ions in a solution have no significant effect on the copper uptake. It could be observed that the highest copper uptake in single component system (copper only) onto treated pine cone fruits was 1.7 mg/g as compared to the highest copper uptake in binary component system (Zn-Cu) was 1.5 mg/g. However for raw pine cone fruits, the highest copper ions in binary solution uptake was 0.94 mg Cu(II) / g of adsorbent compared to uptake in single component of 0.86 mg Cu(II) /g. it is clear from Figure 10 that the presence of zinc has only a very limited effect on the capacity of pine cone fruits for copper.

Multi-component adsorption systems are complicated, because of such factors as the solute-solute competition and the solute-surface interaction involved. Multi-component interactions take place at the active adsorption sites where solid-liquid phase equilibrium occurs. Therefore for each metal present in the multi-component solution, a new position of equilibrium will emerge (showing a different capacity, usually, to the single component state) described by a new set of isotherms constants.[5]

Since any activated carbon has a given surface area, the presence of other adsorbable solutes invariably implies competition for available adsorption sites. Because some adsorption sites can adsorb only certain solutes, not all solutes compete for exactly the same sites.[13]

4.6 Adsorption Isotherms

Equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms (Langmuir and Freundlich). Adsorption equilibrium is established when the concentration of contaminant remaining in solution is in dynamic balance with that at the surface of the solid. It is much affected with the pH, temperature, and other parameters upon the adsorption process.

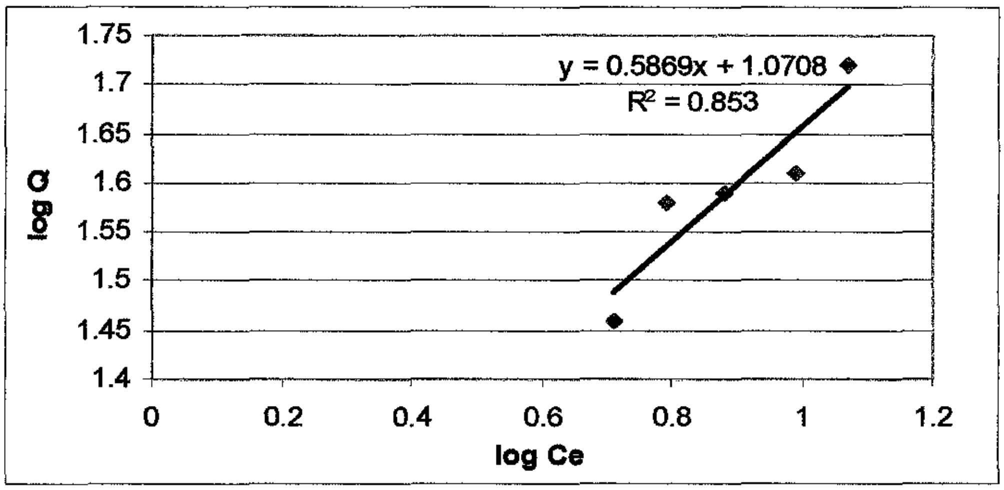

Figure 17: Parameters for Freundlich isotherm

Figure 17 above shows plot of log Q against final concentration of zinc. The values chosen were from experiment carried out at initial concentration of 100 mg/L and 24 hours contact time. The slope of the linear regression is 0.58 and the correlation coefficient is 85%.

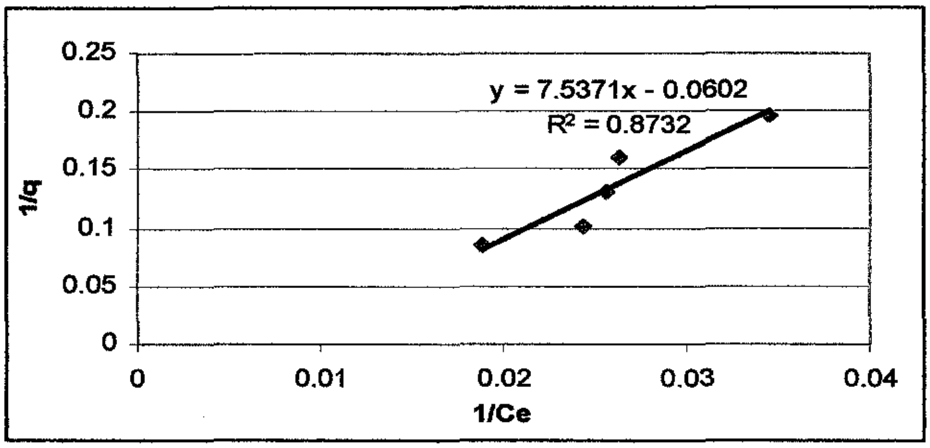

Figure 18: Parameters for Langmuir isotherm

A plot of reciprocal of q against reciprocal of final concentration of zinc solution for experiment carried out at 24 hours and initial concentration of 100 mg/L is illustrated in Figure 18. The plot was carried out to determine parameters for Langmuir isotherm. The linear regression of the values showed correlation coefficient of 87% and slope of 7.5. Due to the higher correlation coefficient value, Langmuir isotherm was selected for isotherm analysis.

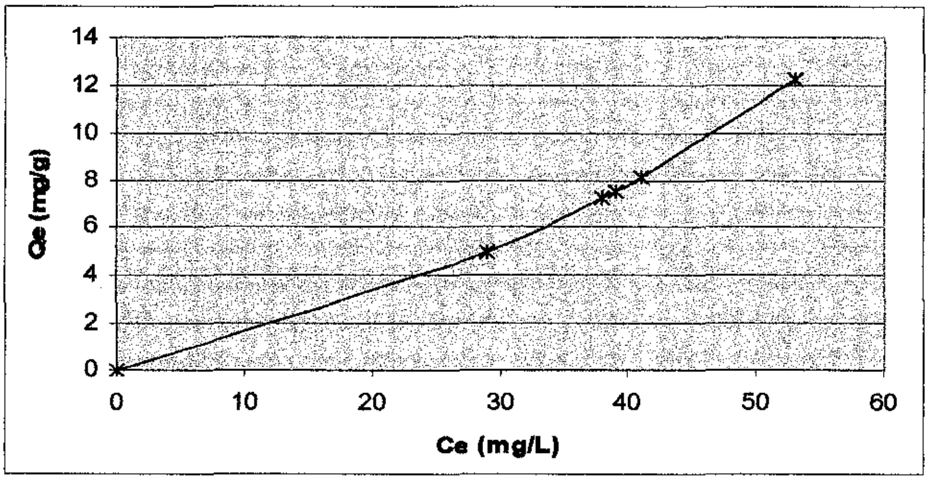

Figure 19: Langmuir isotherm for adsorption of $C_o = 100$ mg/L and contact time 24 hours

The Langmuir isotherm plotted in Figure 19 showed no plateau trend. It may indicate that the equilibrium hasn't been attained yet. The adsorption hasn't reached its optimum rate. More experiments manipulating the initial concentration of metal ions are recommended.

When a solution is contacted with carbon and the system is allowed to attain equilibrium, in that equilibrium state the rate at which molecules are adsorbing to the surface is equal to the rate at which molecules are leaving the surface. This is what the concept of 'equilibrium' implies. That is, equilibrium does not mean that adsorption and desorption cease to occur, but rather that their rates are equal, so that no further net adsorption takes place.[15]

If we define q_o as the value of q in equilibrium with a solution having solute concentration C_o, we can define dimensionless concentrations

$$y = q/q_o \qquad x = C/C_o$$

and write the Langmuir isotherm in dimensionless form as

$$y = \frac{x}{r + (1 - r)x}$$

The parameter r is usually called 'separation factor' because it is similar to separation factors in liquid-liquid extraction and in distillation. For Langmuir isotherm, it can be showed to be equal to $[1/(1+bC_o)]$.

In most adsorption situations with solids like activated carbon, the solute strongly prefers the solid phase over the fluid phase, hence giving good adsorption. If r is greater than 1, the isotherm has a concave shape; it indicates that the solute prefers the fluid phase over the solid phase. This is not very common.[15]

CHAPTER 5

CONCLUSION & RECOMMENDATIONS

5.1 Conclusion

Based on this research, it can be concluded that there is a potential of pine fruit to be used in the industrial sector as an adsorbent for heavy metals removal.

Use of pine fruits in biological treatment system seemed to prevent or reduce toxic impacts to the microorganisms even when the influent metal concentration was slightly higher than the suspected inhibitory levels. This may be useful as an immediate response to toxic upset caused by heavy metals in a biological wastewater treatment plant.

Digestion/activation of pine cone fruits created larger internal surface of the carbon; hence allows more adsorption uptake.

The adsorption of pine cone fruits follows the trend of Langmuir isotherm. For initial concentration of 100 mg/L, the maximum adsorption capacity was 11.75 mg Zn(II) / g of adsorbent after 24 hours of contact time. For initial concentration of 10 mg/L, the maximum adsorption capacity was 0.78 mg of Zn(II) / g of adsorbent after 24 hours contact time.

Co-existence of Zinc with Copper has no significant effect on the copper uptake of the pine cone fruits. Maximum adsorption capacity for copper after 24 hours in copper only and copper-zinc solution was 1.7 and 1.5 mg of Cu(II) /g, respectively.

5.2 Recommendations

Due to constraints of time and the unavailability of the major equipment, several other parameters which may affect the adsorption capability of the activated carbon produced are unable to be carried out. It is recommended to further the research on the effect of different particle size of the pine fruits. Theoretically, smaller particle could increase the contact surface area between the metal ions and the adsorbent which will increase the adsorption uptake. On the other hand, maybe smaller particles of pine fruits is more likely to be degraded compared to the larger particles during the preparation steps to convert it to activated carbon.

The feasibility of using pine fruits in adsorption of heavy metals could be further investigated using adsorption columns. It is important that in batch adsorption tests, initial pH should be controlled to avoid and minimize any precipitation of metals. Additional tests could be carried out using pine fruits to investigate the effect of particle size, synergistic effects and the presence of chelating agents on adsorption of heavy metals.

In addition, the ability of the activated carbon to adsorb common metals exist in the wastewater streams such as chromium, lead etc. should also be investigated.

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APPENDICES

A pinus sylvestris in front of Village 1 Residential College, Universiti Teknologi Petronas

A bunch of pine cone fruits

Pinus sylvestris Linnaeus 1753

Illustration from "Köhlers Medizinal-Pflanzen in naturgetreuen Abbildungen und kurz erläuterndem Texte", Gera, 1883-1914 (Stübers 2001).

Common Names

Scots pine; gemeine kiefer [German]; pin sauvage [French]; skovfyr [Danish]; tall [Swedish]; sosna obyknovennaya [Russian]; bel bor [Bulgarian]; beli bor [Serbian]; beli bor, sumski bor [Croatian]; sosna zwyczajna [Polish]. The term 'Scotch' pine is incorrect and should not be used, as these trees are not a source of that celebrated intoxicant.

Taxonomic notes

Despite its huge range, it is remarkably uniform in its morphology with individual variation within populations much greater than between-population variation. Over 140 subspecies, varieties and forms have been described in what can only be considered botanical nationalism (or madness!), but only the type, var. *sylvestris*, var. *hamata* C. Steven (= subsp. *hamata* (Steven) Fomin), and var. *mongolica* Litvinov (= subsp. *kulundensis* Sukaczev) are now normally accepted (Farjon 1998); even these are barely distinguishable from each other.

Line drawing of var. *mongolica* from the Flora of China (Wu and Raven 1999).

Trees from the extreme west of the range, in NW Scotland (Loch Maree area, Wester Ross), and presumably also the now-extinct Irish populations, show resin chemistry and adaptations to oceanic climates not found in the rest of the species' range. These trees are thought to have survived the ice ages on nunataks off NW Ireland and/or W Scotland, or are possibly derived from Spanish populations (Forrest 1980, 1982; Kinloch et al. 1986); as yet there has been no research as to whether this small endangered population deserves taxonomic recognition. Trees from the rest of Scotland (sometimes treated as var. *scotica* Schott) by contrast showed very close similarity to typical S Swedish / N German origins (Forrest 1980, 1982; Kinloch et al. 1986) and probably colonized across the (then dry) North Sea basin.

Bark (Aust. Con. Soc.).

Some fine photos of the tree and its cones, pollen cones, etc. can be seen: HERE (4-Apr-2004).

Description

A tree to 25-40 m tall and 0.5-1.2 m dbh. Stem straight (contorted only if lead shoot damaged when young, often by pine shoot moth *Evetria turionana*). The crown is variable, with a variety of shapes common in wild populations from level branches to near-fastigiate (Pravdin 1964, Steven & Carlisle 1959); open ovoid-conic when young and usually eventually becoming dense, broadly domed or even flat-topped. Bark on lower stem thick, scaly-plated, grey-brown; on upper stem and branches, thin, flaking, orange-red. Branching uninodal. Shoots green at first, becoming grey-buff by the end of the first summer. Buds ovoid-conic, orange-brown, thinly to occasionally thickly covered in white resin. Leaves in fascicles of two, (2.5-) 4-6 (-9) cm long, 1.5-2 mm wide, always moderately to often strongly glaucous (the only two-leaved hard pine with blue-green or grey-green leaves - an easy pine to identify), longest on vigorous young trees (5-9 cm), short on old trees (2.5-5 cm), commonly slightly twisted, margins finely serrulate; persistent for 2-6 (-9) years; leaf sheath grey, 5-8 mm, slowly eroding to 3-4 mm by leaf senescence. Male cones 8-12 mm, yellow or pink. Cones (2.5-) 3-6 (-7.5) cm long, conic, symmetrical or nearly so, green ripening matt grey-buff to grey-green; mature in November-December, 20 months after pollination, opening from February to April and falling soon after seed shed; scales rhombic, flat to protuberant and (rarely) hooked (with a full range of variation inbetween), with a minutely mucronate dorsal umbo. Seeds black, 4-5 mm, with a 12-20 mm wing (Pravdin 1964, Steven & Carlisle 1959; M.P. Frankis *pers. obs.*).

Var. *hamata* differs mainly in resin chemistry (**Mirov 1967**). It also tends to have more pronounced hooked apophyses than the type usually does, but there is much overlap. The leaves stay a stronger blue-green in winter than the type (which often turns drab green in winter).

Var. *mongolica* differs in having buds more thickly coated in resin, but not all trees show this, and thickly resinous buds can also occur on the type. The foliage tends to be duller, less bluish and more grey-green, to even yellow-grey in winter.

Var. *lapponica* is sometimes distinguished on the basis of shorter and longer-persistent leaves (5-9 years), but its characters overlap and intergrade to such a large extent that it cannot be adequately defined.

Range

Var. *sylvestris* occurs in Europe, from Scotland and Spain eastward, and across N Asia nearly to the Pacific coast. In N Eurasia, from sea level to 1000 m; in S Europe only above 500 m in mountains, to as high as 2400 m in Spanish Sierra Nevada. Absent from E coastal parts of Siberia, rare and local in NE Siberia (Dinets 1998). Native to Croatia. USDA hardiness zone 1-4, depending on origin; Spanish and NW Scottish origins probably zone 6-7. Extinct through human agency (felling, burning, overgrazing) in Ireland, Wales, England, Netherlands and Denmark; re-introduced populations (largely of unknown derivation) thriving locally in all these countries. Also naturalized in SE Canada and NE US (**Little 1980**).

Var. *hamata* is native to the Balkan peninsula, N Turkey and SW Transcaucasia (Dinets 1998), at altitudes of 500-2600 m (**Mirov 1967**). USDA hardiness zone 6.

Var. *lapponica* is often cited as native to Norway, Sweden, Finland, and adjacent parts of Russia north of 65°N (Dinets 1998, **Silba 1986**). It grows to about 30 m tall on the Solovki Islands in the White Sea (Vladimir Dinets e-mail 10-Jan-1998).

Var. *mongolica* is native to Mongolia, NW China, & S. Siberia, at 300-2000 m altitude. It "[o]ccupies great areas in Transbaikalia, in most other areas prefers dry slopes or sandy soils, pure or with *Larix* spp. ('white taiga')" A specimen 42 m tall is known in the Sohondo Nat. Res., Transbaikalia (Dinets 1998). USDA hardiness zone 2.

Dendrochronology

A Jan-1999 search of the Dendrochronology Database (http://tree.ltrr.arizona.edu/cgi-bin/bibliosearch.pl) produced 366 papers involving *Pinus sylvestris*. There are over a hundred citations involving problems in archeology and a like number involving climate studies. It has also been used in studies of stand dynamics, air pollution (including Chernobyl radiation), ecophysiology, and a host of more arcane studies.

This page prepared 2-Jan-1999 by Michael P. Frankis.

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back | ***Pinus*** | **Pinaceae** | **Taxa Home** | **home**

This page is from the Gymnosperm Database
URL: http://www.conifers.org/pi/pin/sylvestris.htm
Edited by Christopher J. Earle
Last modified on 23-Dec-2004

Sample ID	Zn:Flame Actual	Zn:Flame Actual
001	43.5887	NONE
002	43.7254	NONE
003	44.2394	NONE
004	39.9844	NONE
005	42.0537	NONE
006	41.3566	NONE
007	38.2534	NONE
008	39.5967	NONE
009	39.1509	NONE
010	37.4788	NONE
011	38.5233	NONE
012	38.1270	NONE
013	29.4890	NONE
014	27.0654	NONE
015	28.9544	NONE
016	98.3584	NONE

Sample ID	Zn:Flame Actual	Zn:Flame Actual
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002	74.7865	NONE
003	75.2456	NONE
004	67.1204	NONE
005	66.8573	NONE
006	66.9356	NONE
007	61.8755	NONE
008	62.3478	NONE
009	62.0844	NONE
010	63.2466	NONE
011	63.0548	NONE
012	62.8914	NONE
013	53.1044	NONE
014	53.1056	NONE
015	52.7842	NONE
016	99.0458	NONE

Sample ID	Zn:Flame Actual	Zn:Flame Actual
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003	83.9544	NONE
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005	81.0537	NONE
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007	75.2534	NONE
008	74.5887	NONE
009	74.7254	NONE
010	70.2394	NONE
011	69.9844	NONE
012	70.1270	NONE
013	63.4890	NONE
014	64.0654	NONE
015	62.9544	NONE
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Sample ID	Zn:Flame Actual	Zn:Flame Actual
001	92.1098	NONE
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005	86.4367	NONE
006	87.1345	NONE
007	82.2534	NONE
008	81.5887	NONE
009	82.7254	NONE
010	76.2394	NONE
011	75.9844	NONE
012	76.1270	NONE
013	72.0923	NONE
014	71.6893	NONE
015	72.0633	NONE
016	97.7483	NONE

Treating wastewater to armouring eggs

Waste to treat wastewater

Researchers working at the National Centre for Metallurgical Research in Spain have found a way to treat wastewater with steelmaking by-products.

Annually Spain alone generates 44 000 tonnes of rolling mill scale that is extremely difficult to recycle due to its oil content. Heavy metals are toxic pollutants that can accumulate in animal tissues and can cause brain and nerve damage. The researchers hoped that this by-product could remove heavy metals from the wastewater of heavy industries.

The rolling mill scale was powdered and used to treat wastewater contaminated with heavy metals. It was shown to be successful at removing lead, zinc and cadmium from wastewater. However, it cannot be recycled so would need to be buried in a controlled landfill site making it a potential environmental risk.

Enhancing anti-bacterial plastics

The use of antimicrobial plastics has now become commonplace in the food packaging and storage industry. Scientists at the Institute of Polymer Materials, Germany, have been working on new ways to increase the life of the antimicrobial plastics.

They have looked at polyamides impregnated with silver. These polyamides, on interaction with water molecules, release silver ions which can kill bacteria effectively at appropriate levels. The higher the plastic's affinity for water, the higher the level of silver ions released. The researchers examined how crystallinity of the polyamide structure affected its bacteriocidal activity,as the structure of polyamides affects its water uptake. They found that the more crystalline the structure, the poorer its release of silver ions. This should help manufacturers achieve a balance between effective anti-bacterial action combined with long lasting protection.

Clover tackles slug damage

Sclimates and can result in up to a third of a lug damage is a serious problem in temperate wheat crop being damaged, severely reducing yields. Current methods to control slugs involve the use of chemical pellets to kill them. However, these are unreliable in wet conditions, when the pellets can degrade, and kill non-target species such as earthworms and wood mice.

Researchers in the UK may have a solution to the use of chemical pellets – planting clover. The premise is that the clover acts as an alternative and preferable source of food for the slugs so the wheat is left undamaged. Clover, unlike other possible alternative slug food sources, has the added benefits of increasing mineral nitrogen in the soil along with microbial activity and soil stability.

While chemical pellets provided better protection against wheat seed damage, clover performed as well as pellets at protecting wheat seedlings from damage. This raises the possibility of reducing toxic chemicals used in wheat production, while keeping yields at similar levels – something organic agriculture strives to attain.
A laboratory-based comparison of a molluscicide and an alternative food source (red clover) as means of reducing slug damage to winter wheat, Andrew S Brooks, Andrew Wilcox, Richard T Cook, Mitchell J Crook, Pest Management Science, DOI: 10.1002/ps.1056.

Coats protect eggs

Millions of pounds are lost by the egg industry because of poor egg and eggshell quality. Cengiz Caner, a researcher at the University of Turkey, believes even a small decrease in the percentage of eggs damaged could result in a significant reduction in cost to industry.

Eggshells are covered in tiny pores that allow moisture and carbon dioxide to exchange. This porosity shortens the shelf-life of the egg as proteins degrade and water is lost.

To tackle this problem eggs were given an 'edible coating' made up of material such as polysaccharides, proteins and lipids. These coatings increased shelf-life and egg protein freshness and reduced weight loss. The coatings also improved the surface smoothness and glossiness, making them more appealing to consumers.

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Removal of Cd(II) and Pb(II) ions, from aqueous solutions, by adsorption onto sawdust of *Pinus sylvestris*

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Abstract

Fixation of heavy metal ions (Cd(II) and Pb(II)) onto sawdust of *Pinus sylvestris* is presented in this paper. Batch experiments were conducted to study the main parameters such as adsorbent concentration, initial adsorbate concentration, contact time, kinetic, pH solution, and stirring velocity on the sorption of Cd(II) and Pb(II) by sawdust of *P. sylvestris*. Kinetic aspects are studied in order to develop a model which can describe the process of adsorption on sawdust. The equilibrium of a solution between liquid and solid phases is described by Langmuir model. Scanning electronic microscopy (SEM) coupled with energy dispersive X-ray analysis (EDAX) and X-ray photoelectron spectroscopy (XPS) shows that the process is controlled by a porous diffusion with ion-exchange. The capacity of the metal ions to bind onto the biomass was 96% for Cd(II), and 98% for Pb(II). The sorption followed a pseudo-second-order kinetics. The adsorption of these heavy metals ions increased with the pH and reached a maximum at a 5.5 value. From these results, it can be concluded that the sawdust of *P. sylvestris* could be a good adsorbent for the metal ions coming from aqueous solutions. Moreover, this material could also be used for purification of water before rejection into the natural environment.

Keywords: Sawdust; Lead; Cadmium; Adsorption; Kinetic

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1. Introduction

The removal of toxic heavy metals ions from sewage, industrial and mining waste effluents has been widely studied in recent years. Their presence in streams and lakes has been responsible for several health problems with animals, plants, and human beings. Numerous metals such as Sb, Cr, Cd, Pb, Mn, Hg, etc. have toxic effects on man and his environment. The consumption of food containing traces of these elements may lead to various diseases, for example, the consumption of (i) rice containing high concentrations of cadmium (0.37 at 3.6 mg l^{-1}) led to a surge in the Itaï-Itaï disease in Japan in 1955 [1,2], and (ii) fish contaminated with methylmercury led to Minamata disease [3]. For these reasons, the legislation is progressively becoming more stringent; for example, the maximum concentrations of metals in drinking water according to guideline values are now: 0.01 mg l^{-1} for Pb(II) and 0.02 mg l^{-1} for Cd(II) [4]. However, these values are higher due to accumulation phenomena observed when the spreading operations are used instead of direct overflowing into rivers.

Among the many methods available to reduce heavy metals concentrations from wastewater, the most common are chemical precipitation, ion-exchange, and reverse osmosis. Precipitation methods are particularly reliable but require large settling tanks for the precipitation of voluminous alkalines sludges and a subsequent treatment is needed [5]. Ion-exchange has the advantage of allowing the recovery of metallic ions, but it is expensive and sophisticated. This has encouraged research into discovering materials that are both efficient and cheap. The by-products and wastes from the agricultural and forest industries were studied as these materials could be assumed as low-cost since they (i) require little processing and (ii) are abundant in nature. Commonly, it concerns vegetal materials, then the term of biosorption is used to designate the fixation of contaminants onto biomaterials. The low-cost adsorbent used in our study is the sawdust of *Pinus sylvestris*, a by-product of the wood industry. It contains various organic compounds (lignin, cellulose, and hemicellulose) with polyphenolic groups that might be useful for binding heavy metals ions [6].

The objective of this preliminary study was to investigate the feasibility of metallic ions removal from aqueous solution by sawdust of *P. sylvestris*. The kinetics of the process was determined, especially in relation to the effects of various factors on the removal. The factors investigated included aqueous metallic concentration, stirring, contact time, pH of solution, and adsorbent concentration. The mechanism of metallic ions adsorption at sawdust–solution interface was also studied.

2. Materials and methods

2.1. Adsorbate

All the compounds used to prepare reagent solutions were of analytic reagent grade. The mother solution of Cd(II) and Pb(II) (1000 mg l^{-1} for each ion) is prepared by dissolving a weighed quantity of the respective nitrate salts in twice distilled water. The concentrations of metals solutions ranged from 1 to 10 mg l^{-1}. Before mixing with the sawdust, the pH of each solution was adjusted to the required value for the sorption of Cd(II) and Pb(II) ions, by adding 0.1 M NaOH or 0.1 M HNO_3. Constant ionic strength (0.01 M NaCl) was used in all experiments.

2.2. Adsorbent

The sawdust of *P. sylvestris* used as adsorbent was provided by the Société d'Exploitation Forestière Barillet, Châteauneuf-sur-Loire 45, France. For the laboratory studies only, the sawdust was washed several times with twice distilled water to remove surface impurities. The process was followed by air drying at 110 °C for 24 h. The sawdust was ground and sieved into three sizes: 0.1–0.16, 0.16–0.2, and 0.2–0.25 mm.

For laboratory scale experiments and to prevent the elution of phenolic compounds, which would stain the treated water, the ground sawdust was treated with formaldehyde in an acidic medium [7] under conditions previously optimized by Vázquez et al. [8]: a 1:4 (v/v) mixture of 37% formaldehyde and 0.2 M H_2SO_4 was heated to 50 °C, 4 g of sawdust per 10 ml of formaldehyde were then added and stirred at 50 °C for 2 h. The sawdust was filtered off, washed with distilled water until the pH of the washing was 6 and finally air-dried. In the case of industrial waste, it was shown that this treatment was not necessary [9].

To identify the active sites on the sawdust surface, the biomass was characterized by different methods such as IR, XPS, MEB coupled with EDAX, potentiometric and conductimetric titrations. Identification of the active sites is a way to find the mechanisms possibly involved in the process (physical adsorption, complexation, ionic exchange, and surface micro-precipitation). Analysis of these experimental results showed the influence of pH on the deprotonation of functional groups of sawdust. These results will be discussed in Section 3.3.

2.3. Analysis of Pb(II) and Cd(II) ions

A Hitachi Z8270 (Perkin-Elmer, France) atomic Absorption Spectrophotometer equipped with a Zeeman atomizer and a SSC-300 autosampler was used to determine the concentration of unadsorbed Pb(II) and Cd(II) ions in the effluent. Zeeman effect correction and pyrolytic graphite-coated tubes were used for AAS measurements. All the instrumental conditions were optimized for maximum sensitivity as indicated by the manufacturer.

The surface structure of sawdust was analyzed by scanning electronic microscopy (SEM) coupled with energy dispersive X-ray analysis (EDAX) using the Cambridge-Leo system at 15 kV with background subtraction with a summation of 240 scans. For these analyses sawdust samples were mounted on a stainless steel stab using a double-stick tape, coated with a thin layer of gold.

The evaluation of the surface characteristics was performed by X-ray photoelectron spectroscopy (XPS) using an ESCA-Auger system (Perkin-Elmer, Physical Electronics Division). XPS spectra were taken before and after lead and cadmium sorption to identify the groups involved in the sorption.

2.4. Batch sorption experiments

The experiments were performed in a batch reactor at 20.5 ± 0.5 °C with continuous stirring fixed at 400 rpm. Biosorbent particles (0.1–2 g) were left in contact with 100 ml of each solution (1–50 mg l^{-1}) during 1 h; the initial pH value of the solution was adjusted with nitric acid (0.1 mol l^{-1}) or sodium hydroxide (0.1 mol l^{-1}). The pH value was chosen so that the metallic species were present in their divalent form.

Aliquots of supernatant were withdrawn at different time intervals and the amount of metallic ions in the solution was estimated by atomic absorption. In order to obtain the sorption capacity, the amount of ions adsorbed per mass unit of biomass (q_e in milligram of metal ions per gram of sawdust) was evaluated using the following expression (1):

$$q_e = \frac{C_0 - C_e}{m} \times V \tag{1}$$

where C_0 is the initial metal ions concentration (mg l^{-1}), C_e the equilibrium metal ions concentration (mg l^{-1}), V the volume of the aqueous phase (l), and m is the amount of the sawdust used (g). Sorption efficiency (ε) is considered in percentage as

$$\varepsilon = 100 - 100 \times \frac{C_e}{C_0} \tag{2}$$

For each condition, three experiments were performed and the deviation (Δq_e) of q_e, during the investigations, was calculated from Eq. (3) as follows:

$$\Delta q_e\,(\%) = \frac{\sum_{i=1}^{N} |[(q_e, i)_{cal} - (q_e, i)_{exp}]/(q_e, i)_{exp}|}{N} \times 100 \tag{3}$$

where the subscripts “exp” and “cal” show the experimental and calculated values of q_e and N is the number of measurements.

2.5. Diffusion models

Kinetics studies of sorption are significant since (i) the data can be used for determining the time required to reach equilibrium, (ii) the rate of adsorption can be used to deduce predictive models for column experiments, and (iii) these studies can be used in understanding the influence of variables on the sorption of solutes.

It is important to study the rate at which metallic ions can be removed from aqueous solutions in order to apply adsorption to wastewater treatment. There are essentially four stages in the adsorption process by porous adsorbents [10]: (i) solute transfer from the bulk solution to the boundary film bordering the polymer surface, (ii) solute transport from boundary film to the sorbent surface, (iii) solute transfer from the sorbent surface to the intraparticular active sites, and (iv) interactions of the solute molecules with the available sites on the internal surface.

One or more of the four above-mentioned steps may control the rate at which the solute is adsorbed and the amount of solute that is adsorbed onto the solid particles; at low stirring speeds, the boundary layer resistance will be significant and step (ii) will be important in the rate controlling process.

External mass transfer is characterized by the initial rate of solute sorption [10]. It can be calculated from the initial slope of the curves C_t/C_0 versus time. Intraparticular diffusion is characterized by the relationship between specific sorption (q_t) and the square root of time ($\sqrt{t}$). This relation was given by Weber and Morris as cited in [11,12]:

$$q_t = \frac{k_w}{m} t^{1/2} \tag{4}$$

where m is the mass of adsorbent (g), q_t the amount of metal ions adsorbed at time t (mg g^{-1}), and k_w is the initial rate of intraparticular diffusion (mg l^{-1} s$^{-0.5}$).

3. Results and discussion

3.1. Effect of biomass pre-treatment on Cd^{2+} and Pb^{2+} sorption

The effect of the treatment on the sorption was examined by using the experimental procedure previously described. The solution with an initial concentration of 100 mg l^{-1} was stirred with 1 g l^{-1} of treated sawdust. Another experiment was carried out with untreated sawdust. The pH of each solution was regulated by adding dilute NaOH or HNO_3. Table 1 shows the retention capacities of treated sawdust and untreated sawdust for lead and cadmium ions sorption after a contact time of 1 h.

The results show that the removal yield for the metals studied is not modified by a preliminary treatment of the biomass. But this processing favors the stabilization of the extractable compounds of wood. Chemical treatment induces a stabilization of the hydrosoluble compounds of wood by creating covalent bonds on the constitutive units, and makes the biosorbent able to adsorb metal cations without an increase in COD that is due to the release of the polyphenolic compounds.

3.2. Effects of contact time and initial metal ion concentration

To establish an appropriate contact time between the biomass and metallic ions solution, sorption capacities of metal ions were measured as a function of time. As shown in Figs. 1 and 2, lead and cadmium were rapidly removed by sawdust (less than 20 min). This is rather good as compared with the results obtained with other adsorbents referred to other papers (Table 2). For the following experiments, the contact time was maintained for an hour to ensure that equilibrium was really achieved.

The equilibrium sorption capacity of the biomass for Cd(II) and Pb(II) ions increased with a rise in the initial ions concentration from 80 ± 1.8% up to 95 ± 0.5% for Cd(II) and 84 ± 1.8% up to 98 ± 0.5% for Pb(II), as it also is shown in Table 3. Ion removal is highly concentration-dependent. On the contrary, it may be noticed from Figs. 1 and 2 that time to reach equilibrium is concentration-independent.

Table 1
Effect of biomass pre-treatment on Cd^{2+} and Pb^{2+} sorption after 1 h of contact time

Adsorbent	COD (mg O_2 l^{-1})	Removal of Cd^{2+} (%)	Removal of Pb^{2+} (%)
Untreated sawdust	28	96.2	97.5
Sawdust treated with H_2SO_4 and HCHO	8	96.0	97.6

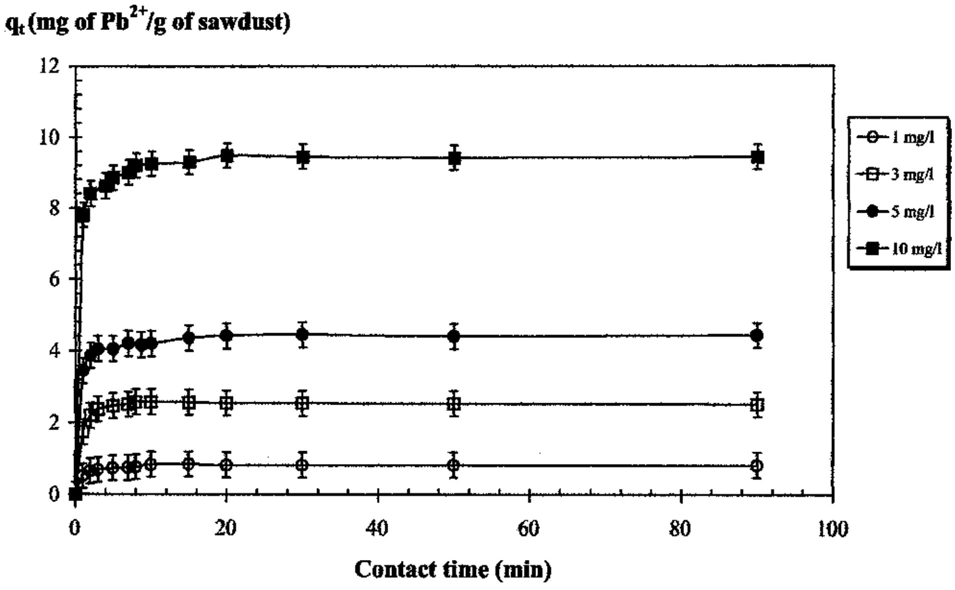

Fig. 1. Influence of contact time on the sorption capacity of Pb(II) onto sawdust of *Pinus sylvestris* at different initial concentrations (*T*, 25 °C; stirring speed, 400 rpm; pH, 5.5; *m*, 0.1 g of sawdust).

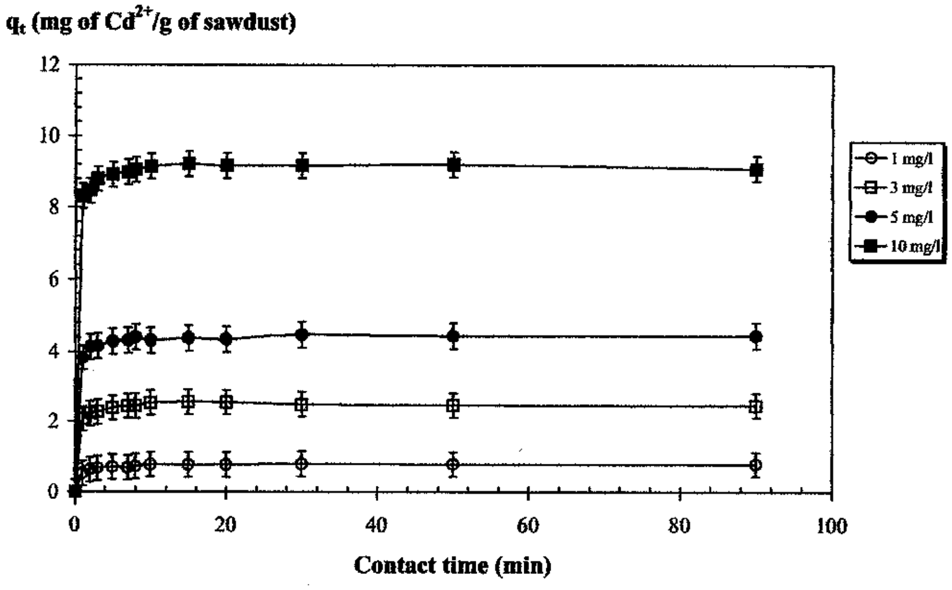

Fig. 2. Influence of contact time on the sorption capacity of Cd(II) onto sawdust of *Pinus sylvestris* at different initial concentrations (*T*, 25 °C; stirring speed, 400 rpm; pH, 5.5; *m*, 0.1 g of sawdust).

Table 2
Contact time for different adsorption systems

Metallic ions solution	Adsorbent	Contact time (min)	References
Pb(II)	Polyacrylamide grafted sawdust	180	Raji and Anirudhan [13]
Cd(II), Hg(II)	Treated *Pinus pinaster* bark	120	Vázquez et al. [14]
Cu(II)	Sawdust from India	60	Vaishya and Prasad [15]
Cd(II)	Poly(vinylalcohol)-coated/cibacron blues F3GA-attached polypropylene hollow fiber membranes	40	Büyüktuncel et al. [16]
Cd(II)	Actinomycetes	5	Kefala et al. [17]
Fe(III)	*Zoogloea ramigera* and *Rhizopus arrhizus*	15	Sa and Kutsal [18]
Cr(III), Cr(IV), Ni(II)	Industrial biomass with reference to environmental control	30	Sekhar et al. [19]
Cd(II), Pb(II), Fe(III)	*Schizomeris leibleinii*	25	Özer et al. [20]
Pb(II), Cu(II), Ni(II)	Low cost natural polysaccharides	20	Gérentes et al. [21]
Pb(II)	*Streptomyces pilosus*	5	Sadowski et al. [22]

This increase in loading capacity of the biosorbent with relation to metal ions concentration is probably due to a high driving force for mass transfer. In fact, the more concentrated the solution is, the better the adsorption is. At 20 °C, when the initial metal ions concentration was increased from 1 to 10 mg l^{-1}, the loading capacity of dried sawdust increased from 0.84 ± 0.13 to 9.49 ± 0.2 mg of Pb per gram of sawdust (Fig. 1) and 0.80 ± 0.13 to 9.29 ± 0.2 mg of Cd per gram of sawdust, respectively (Fig. 2).

It is well known [23,24] that the rate of the sorption process is modified by several parameters such as stirring speed, the structural properties of the adsorbent (i.e. porosity, specific area, particle size, etc.), the properties of the metallic ions (ionic radius, number of coordination, and speciation), metallic ions concentration, chelates formation between metallic ions, and the adsorbent, etc. This is why intraparticular diffusion was also studied in this work. The model chosen refers to the theory reported by Weber and Morris [24]. Temperature and stirring speed were constant for all experiments. The experimental results of this model demonstrated a non-linear distribution of points. The double nature of the plots (*curved and linear*) was obtained for the sorption process at different initial concentrations (Fig. 3); this indicated the existence of an intraparticular diffusion in this process. The initial

Table 3
Sorption capacity of metallic ions at different initial concentrations

Initial concentration (mg l^{-1})	Sorption capacity of Pb(II) (%)[a]	Sorption capacity of Cd(II) (%)[a]
1	84	80
3	86	84
5	89	88
10	98	95

Conditions: *T*, 25 °C; stirring speed, 400 rpm; pH, 5.5; *m*, 0.1 g of sawdust.

[a] The sorption capacity was calculated according to Eq. (2).

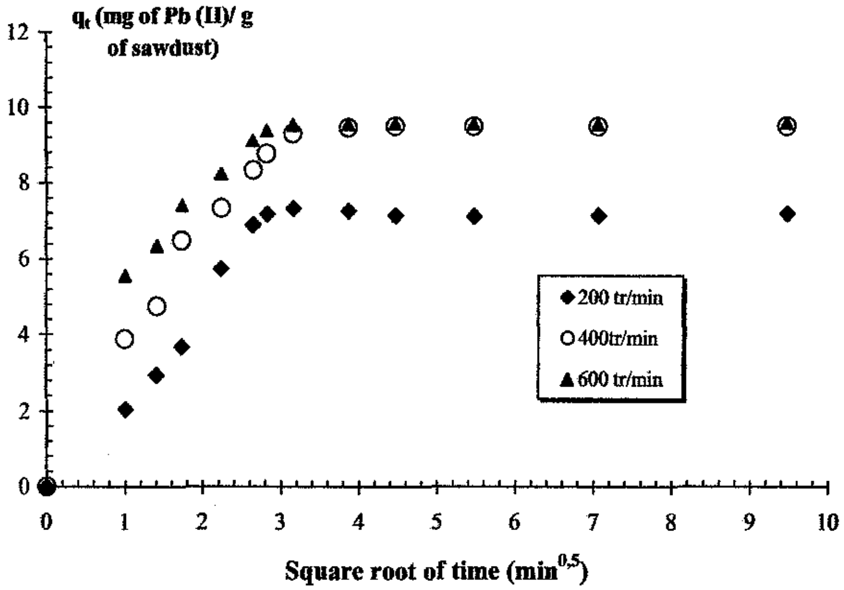

Fig. 3. Effect of stirring speed on the sorption capacity of Pb(II) onto sawdust of *Pinus sylvestris* (particular size, 0.1–0.16 mm; T, 25 °C; pH, 5.5; C_0, 10 mg l^{-1}; m, 0.1 g of sawdust).

portion represents the film diffusion. The subsequent linear portion is characteristic of an intraparticular diffusion. Similar results were found by Gaid et al. [25], Saucedo et al. [26], and Ho et al. [11]. These results also show that the biosorbent can easily replace the physical adsorbent.

3.3. Effect of pH

The pH of the aqueous solution is an important controlling parameter in the adsorption process [27]. Thus, the effect of hydrogen ion concentration was examined from solutions at pH ranging from 2 to 9. Fig. 4 summarizes the uptake of Cd(II) and Pb(II) onto sawdust of *P. sylvestris* at various pH values. The maximum uptake of these ions was obtained at about pH 5.5.

At lower pH values, the H_3O^+ ions compete with the metal ions for the exchange sites in the sorbent. There is an increase in metal ions uptake as the pH value increases from 2 up to 5. One of the reasons for the metal ions adsorption behavior of the biosorbent is that the sawdust surface contains a large number of active sites. The metal uptake depends on these active sites as well as on the nature of the metal ions in solution. In fact, at pH lower than pH_{zpc} values (pH at zero point charge), complexation phenomena can also occur, especially for the carboxylic groups. In other respects, the property of the sawdust to uptake metal ions can also be explained by the carbonyl groups (C=O) or the hydroxyl groups (OH) of polyphenols. The oxygen of each carbonyl and hydroxyl group is considered as a strong Lewis base because of the presence of its vacant doublet electrons. Thanks to this

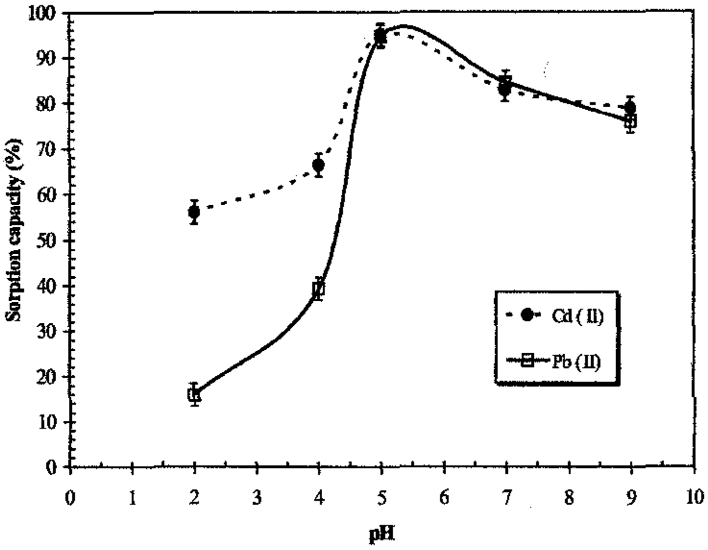

Fig. 4. Uptake of Cd(II) and Pb(II) onto sawdust of *Pinus sylvestris* at various pH values (C_0, 5 mg l^{-1}; T, 25 °C; m, 0.1 g of sawdust). The pH was regulated with a minimal amount of 0.1 M of NaOH or HNO_3.

doublet, the oxygen base makes a complex of coordination with the chemical entities low in electrons (metal ions, for example) (Fig. 5).

When pH increases from acid value to a neutral value, various species are noticeably present (for example, at pH 6, different sorts of species are present in each solution, i.e. $Pb(OH)^+$ and Pb^{2+} for the solution of lead and only Cd^{2+} for the solution of cadmium as suggested by Stumm and Morgan [28]). The affinities of the surface sites of sawdust depend on the nature of ions. This may be further explained in relation to a competition effect between the H_3O^+ and metal ions. At low pH values, the concentration of H_3O^+ ions is largely superior to that of the metal ions, hence the former ions occupy the binding

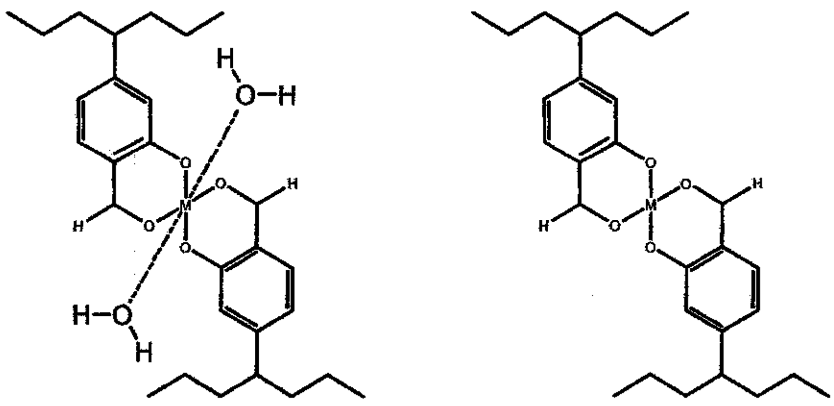

Fig. 5. Formation of metal complexes with the functional groups on the sawdust surface.

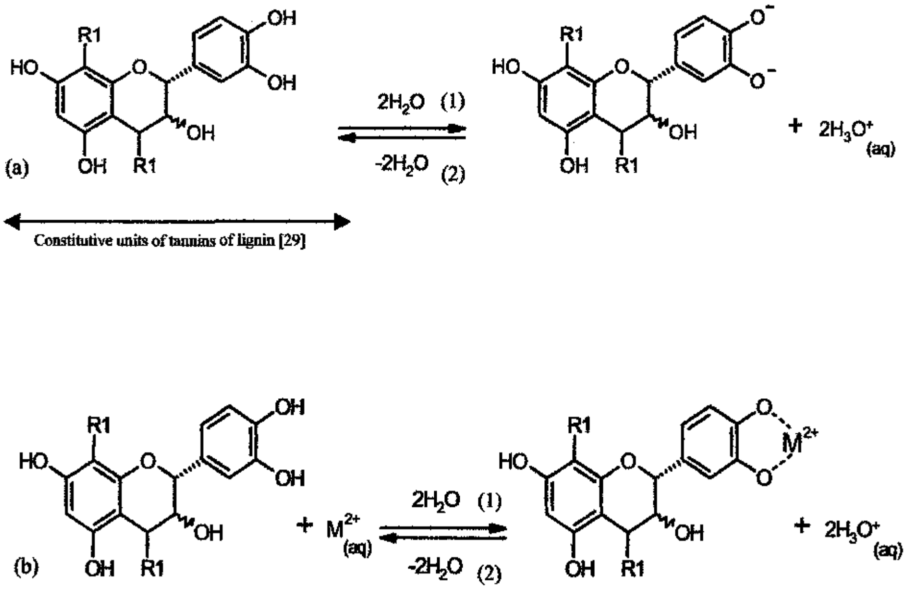

Fig. 6. Mechanism of biosorption: (a) represents the first stage of ion-exchange (deprotonation), while (b) shows the attachment (adsorption) of the metal cations onto the deprotonated active sites on the sawdust surface [29]. The symbol M is a metal ion of charge 2+.

sites on the sawdust, leaving metal ions free in solution. When the pH is increased, the concentration H_3O^+ ions decreases, and the sites on the sawdust surface mainly turn into dissociated forms (Fig. 6a) and can exchange H_3O^+ ions with metallic ions in solution (Fig. 6b). For all subsequent experiments, a pH of 5.5 was used in order to ensure that Cd(II) and Pb(II) do not precipitate as hydroxide.

3.4. Sorption isotherm

Since solution pH has a significant effect on adsorption equilibrium, the Langmuir model [30] was applied to the sorption equilibrium at different pH in order to establish the maximum metal sorption capacity. The equilibrium removal of the Pb(II) and Cd(II) ions can be mathematically expressed by the adsorption isotherms, according to the Langmuir model (5).

$$q_e = q_m \frac{bC_e}{1 + bC_e} \tag{5}$$

or its linearized form (6)

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b} \tag{6}$$

where C_e is the equilibrium aqueous metal ions concentration ($\mathrm{mg\,l^{-1}}$), q_e the amount of metal ions adsorbed per gram of sawdust at equilibrium ($\mathrm{mg\,g^{-1}}$), q_m and b the Langmuir

Table 4
Langmuir adsorption constants obtained from the isotherms of solutions of Pb(II) and Cd(II) at different initial pH

pH	Langmuir constants									
	Pb(II)					Cd(II)				
	q_e (mg g^{-1})	q_m (mg g^{-1})	b (l mg^{-1})	R_L	R^2	q_e (mg g^{-1})	q_m (mg g^{-1})	b (l mg^{-1})	R_L	R^2
4	7.17	15.77	0.058	0.63	0.92	6.29	15.27	0.054	0.65	0.95
5	9.78	22.22	0.052	0.66	0.91	9.29	19.08	0.057	0.64	0.93
7	3.90	8.45	0.077	0.56	0.99	5.5	6.72	0.105	0.49	0.99

R^2 is the correlation coefficient.

constants related to the maximum adsorption capacity and energy of adsorption, respectively. The values of b and q_m can be determined from the linear plot of C_e/q_e versus C_e. The main characteristic of Langmuir isotherm is its dimensionless constant separation factor (equilibrium parameter), R_L, defined by $R_L = 1/(1 + bC_0)$ [31].

The sorption isotherms were determined at different pH values for a concentration range of 1–50 mg l^{-1}. All solutions contained a fixed mass of sawdust (1 g of sawdust per liter of solution). The q_m, b, and R_L values calculated from isotherms at different initial pH values are presented in Table 4. The plots of C_e/q_e versus C_e obtained for two metals are linear (Figs. 7 and 8) according to the Langmuir model.

The values of q_m and b were determined from Eq. (6) and found to be 22.22 mg of Pb per gram of sawdust and 19.08 mg of Cd per gram of sawdust, under optimum adsorption conditions.

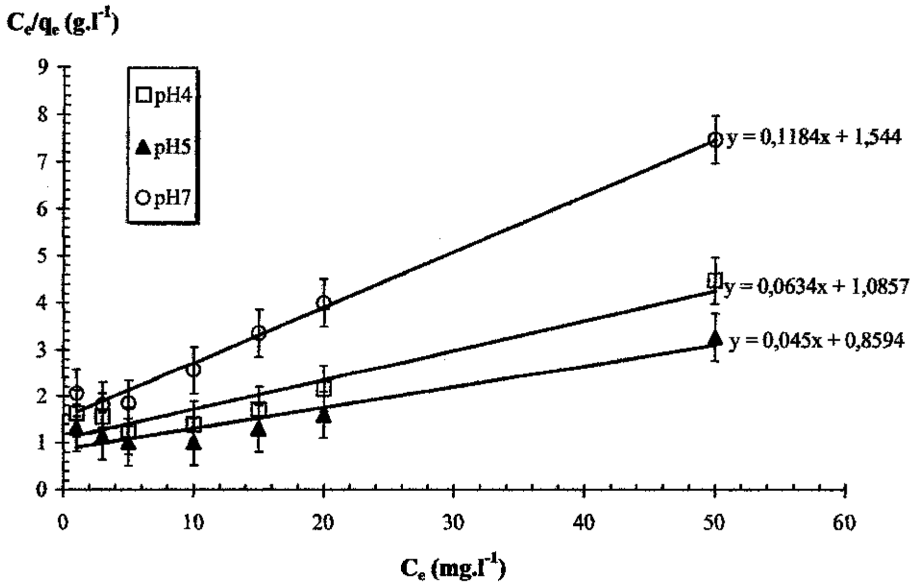

Fig. 7. Equilibrium isotherms at different pH for adsorption of Pb(II) ions onto sawdust of *Pinus sylvestris* (T, 25 °C; m, 0.1 g of sawdust; stirring speed, 400 rpm).

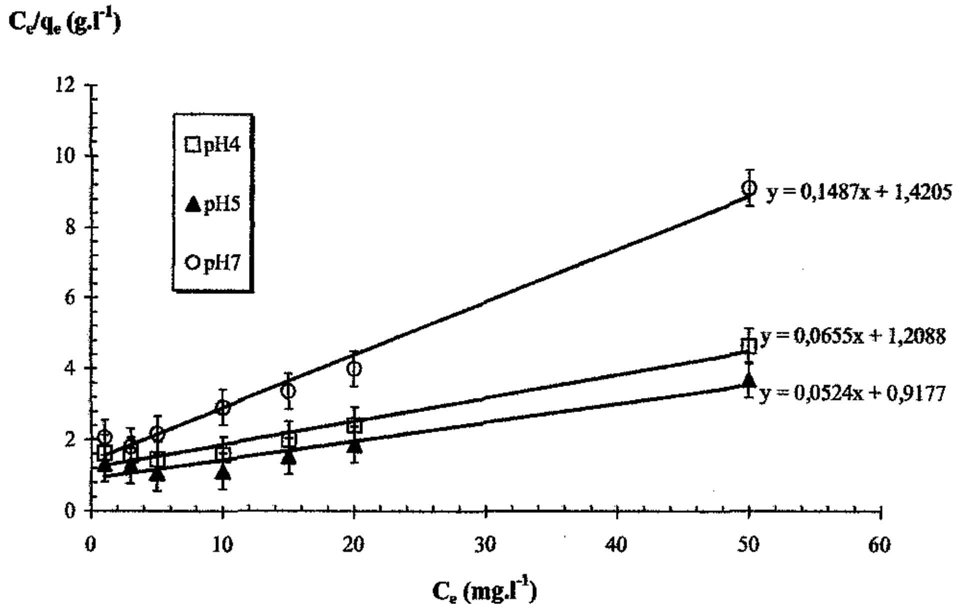

Fig. 8. Equilibrium isotherms at different pH for adsorption of Cd(II) ions onto sawdust of *Pinus sylvestris* (*T*, 25 °C; *m*, 0.1 g of sawdust; stirring speed, 400 rpm).

The sorption of Pb(II) and Cd(II) ions onto sawdust may be due to the development of a free negative charge on the surface. Besides, sorption of the above-mentioned metals may be due to ion-exchanges at the surface level or attachment through hydrogen bonding. The more electronegative a metal is, the better its sorption is. Sawdust exhibited better sorption capacity for Pb(II) (1.55 on Alfred and Rochow scale) than for Cd(II) (1.46 on Alfred and Rochow scale) [32].

However, q_e has smaller values than q_m. This shows that the adsorption of Cd(II) and Pd(II) ions onto sawdust is a monolayer type one that does not fully cover the surface of the sawdust [33]. Moreover, the R_L values obtained range from zero to one in the range of zero and one. According to McKay [31] and Battacharya and Venkobachar [34], this indicates that the sorption of Pb(II) and Cd(II) onto sawdust is feasible at the concentrations studied. The results also show the variation of *b* according to pH. This variation underlines the fact that the affinity of metal ions onto sawdust is pH-dependent.

3.5. Sorption kinetics

In order to determine the sorption kinetics of Pb(II) and Cd(II) ions, the first-order and second-order kinetics models were checked. The first-order rate expression of Lagergren [32] based on solid capacity is generally expressed as follows:

$$\frac{dq_t}{dt} = k_{1,\mathrm{ad}}(q_e - q_t) \tag{7}$$

where q_e and q_t are the amounts of metal ions adsorbed onto the sawdust (mg g^{-1}), respectively, at equilibrium and at time t and $k_{1,\mathrm{ad}}$ is the rate constant of first-order (min^{-1}). After integration in boundary conditions ($t = 0$ to t and $q_t = 0$ to q_e), Eq. (7) becomes

$$\log(q_e - q_t) = \log q_e - \frac{k_{1,\mathrm{ad}}}{2.303}t \tag{8}$$

In most cases, the first-order equation of Lagergren did not apply well throughout the whole range of contact times and is generally applicable over the initial 20–30 min of the sorption process. The plotting of $\log(q_e - q_t)$ versus "time" (curves not shown) deviated considerably from the theoretical data after a short period. The plots and intercepts of curves were used to determine the first-order constant $k_{1,\mathrm{ad}}$ and equilibrium capacity q_e. The calculated values of q_e (Table 5) from the first-order kinetics model are lower than the experimental ones. So the sorption system does not follow a first-order reaction.

The pseudo-second-order equation, which is based on the sorption capacity of solid phase, was also used. If the rate of sorption is a second-order mechanism, the pseudo-second-order chemisorption kinetics rate equation is expressed as [35]:

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_{2,\mathrm{ad}}(q_e - q_t)^2 \tag{9}$$

where $k_{2,\mathrm{ad}}$ is the rate constant of second-order biosorption (g mg^{-1} min^{-1}). For boundary conditions ($t = 0$ to t and $q_t = 0$ to q_e), Eq. (9) becomes

$$\frac{t}{q_t} = \frac{1}{k_{2,\mathrm{ad}}q_e^2} + \frac{1}{q_e}t \tag{10}$$

Using Eq. (10), t/q_t was plotted versus t at different adsorbent concentrations and second-order sorption rate constant ($k_{2,\mathrm{ad}}$) and q_e values were determined from the slopes and intercepts of the plots (Figs. 9 and 10). The correlation coefficients for the linear plots are superior to 0.999 in all the systems. The values of these parameters and the deviation are presented in Table 5. The theoretical q_e values agree perfectly with the experimental q_e values. This suggests that the sorption system is not a first-order reaction and that a pseudo-second-order model (Eq. (10)) can be considered. The latter is based on the assumption that the rate limiting step may be a chemical sorption involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate. It provides the best correlation of the data.

3.6. *Effect of stirring speed*

The quality of the dispersion of the solid in adsorption on a batch reactor is a significant factor as in all processes of mass transfer. Stirring influences the distribution of the aqueous solution and can also act on the formation of an external film of separation. Table 6 shows the various values of the constants of diffusion according to stirring velocity (Spahn and Schlünder coefficient, k_s [36] is assigned to external diffusion and the k_w coefficient to intraparticular diffusion, according to Morris and Weber [24]). The results show that an increase in stirring speed from 200 to 600 rpm does not significantly modify the coefficient of diffusion of metal ions on the sawdust. It can be assumed

Table 5

Comparison of the first- and second-order adsorption rate constants, for calculated ($q_{e,cal}$) and experimental ($q_{e,exp}$) values at different adsorbent concentrations[a]

Metallic ion	Adsorbent concentration (g/100 ml)	First-order kinetic model				Second-order kinetic model		
		$q_{e,exp}$ (mg g^{-1})	$k_{1,ad}$ (min^{-1})	$q_{e,cal}$ (mg g^{-1})	Deviation (%)	$k_{2,ad}$ (g mg^{-1} min^{-1})	$q_{e,cal}$ (mg g^{-1})	Deviation (%)
Cd(II)	0.1	9.29	0.007	0.18	98.0	1.22	9.10	2.1
	0.5	1.95	0.015	0.13	93.4	10.89	1.94	0.1
	1	0.99	0.024	0.06	94.2	18.31	0.98	0.4
Pb(II)	0.1	9.49	0.010	0.09	99.0	0.51	9.45	0.4
	0.5	1.97	0.012	0.06	97.1	8.53	1.96	0.5
	1	1.00	0.035	0.03	97.3	9.27	0.99	0.5

[a] The deviation was calculated according to Eq. (3).

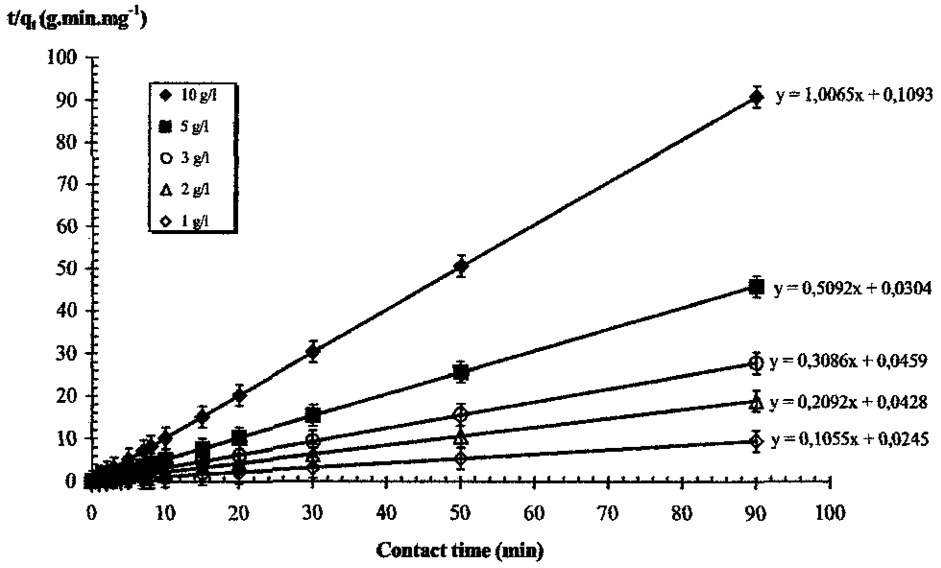

Fig. 9. Plot of Pb(II) for the pseudo-second-order kinetic model at different adsorbent concentrations (*T*, 25 °C; stirring speed, 400 rpm; pH, 5.5; C_0, 10 mg l^{-1}).

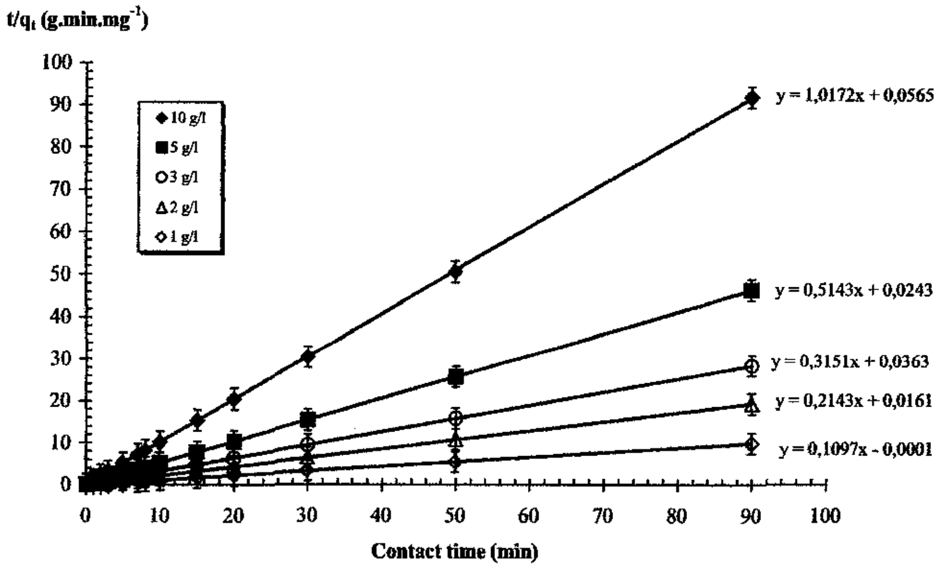

Fig. 10. Plot of Cd(II) for the pseudo-second-order kinetic model at different adsorbent concentrations (*T*, 25 °C; stirring speed, 400 rpm; pH, 5.5; C_0, 10 mg l^{-1}).

Table 6
Effect of stirring speed on diffusion coefficients k_w and k_s

Stirring speed (rpm)	Constant of external diffusion[a], k_s ($\times 10^{-8}$ m s^{-1})	Constant of intraparticular diffusion[b], k_w (mg g^{-1} s$^{-0.5}$)
Cadmium		
200	1.89	0.31
400	4.33	0.41
600	4.33	0.45
Lead		
200	1.95	0.30
400	3.03	0.36
600	3.03	0.39

[a] This diffusion coefficient was calculated from $C_t/C_0 = f(t)$ according to Spahn and Schlünder models [36].
[b] This diffusion coefficient was calculated from $q_t = f(\sqrt{t})$ according to Weber and Morris models [24].

that the rate of adsorption is controlled by the diffusion of the solute inside the biomass [24].

However, the coefficient of external diffusion is rather different in the case of Pb(II). Therefore, the effect of stirring is obscured by the effect of an external resistance to mass transfer inside the solid particle.

3.7. Analysis of sawdust by SEM, EDAX, and XPS

Electron micrographs and EDAX spectra of the sawdust before and after sorption with 100 mg l^{-1} of solution, which contained Pb(II) and Cd(II), are shown in Figs. 11–15. These

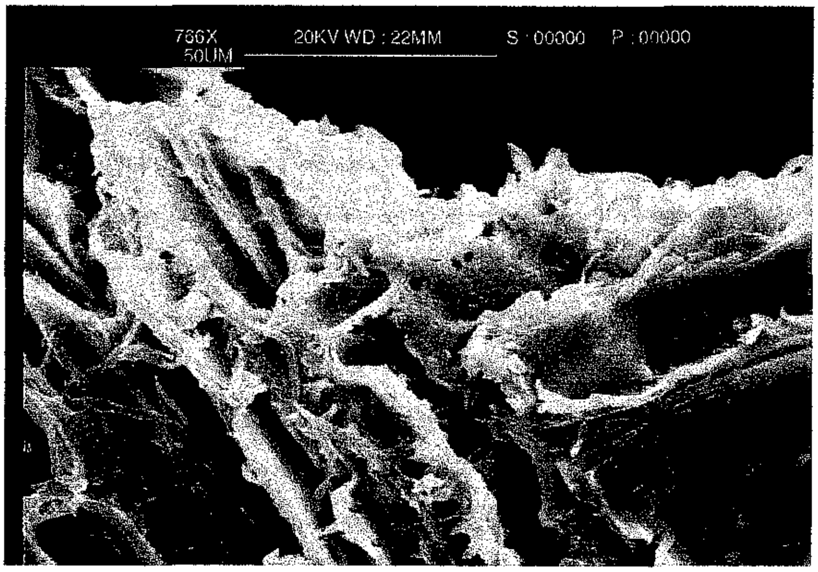

Fig. 11. Typical SEM micrograph of virgin sawdust of *Pinus sylvestris*.

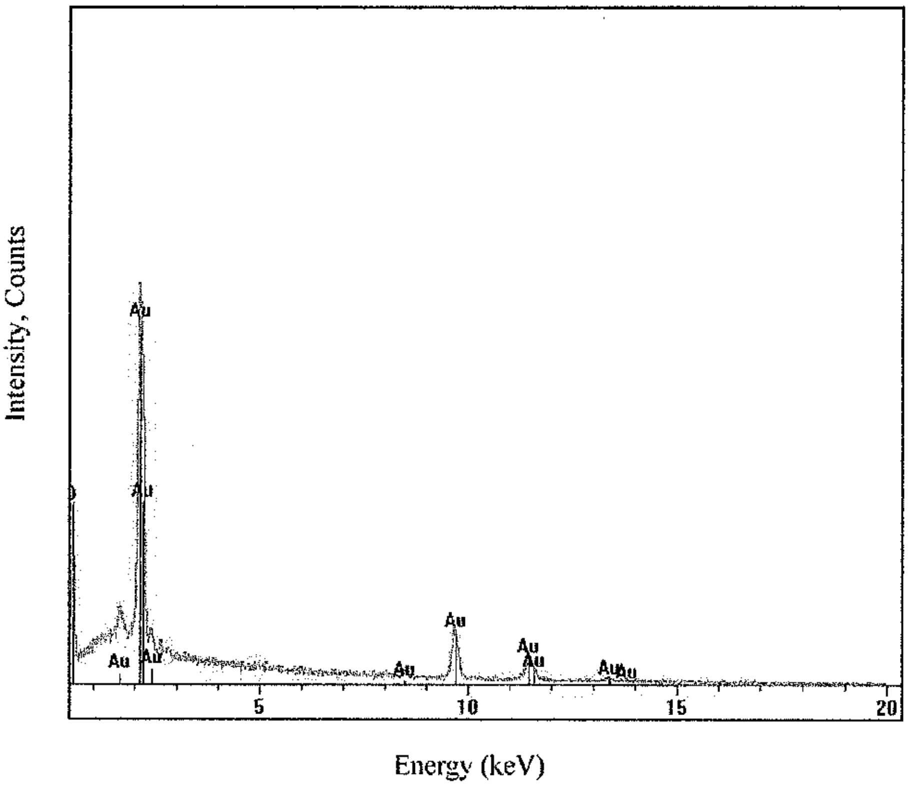

Fig. 12. Corresponding EDAX spectrum of virgin sawdust of *Pinus sylvestris*.

micrographs reveal clearly the apparition of pellets on the sawdust particles (Figs. 13 and 14), whereas these pellets were absent on the sawdust before loading it with metallic ions solution (Fig. 11). Some modifications can be observed on the sawdust particles after adsorption with: (i) a strong density of pellets on the sawdust particles (Fig. 13), (ii) pellets inside layers of sawdust particles (Fig. 14), and (iii) two types of crystals looking like "rice seeds" (Fig. 13) and "billiard balls" (Fig. 14).

The density of pellets observed in SEM was also characterized by EDAX. The EDAX analysis reveals Pb(II) and Cd(II) signals on the surface of the sawdust after adsorption by a metallic ions solution (Fig. 15). The presence of gold peaks in all spectra results from the gold purposely settled to increase the electric conduction and to improve the quality of the micrographs.

The XPS spectra obtained before (a) and after (b) Pb(II) biosorption onto sawdust are presented in Figs. 16 and 17. Fig. 16 shows that doublets characteristic of lead appear, respectively, at 138.5 eV (assigned to Pb $4f_{7/2}$) and at 143.85 eV (assigned to Pb $4f_{5/2}$) after loading sawdust with Pb(II) solution. The peak observed at 138.5 eV agrees with the 138.0 eV value reported for PbO [37]. This shows a fixation of lead onto sawdust during the process. A similar mechanism was also made for the cadmium uptake. There is also a significant difference between the oxygen peaks before (a) and after (b) lead biosorption

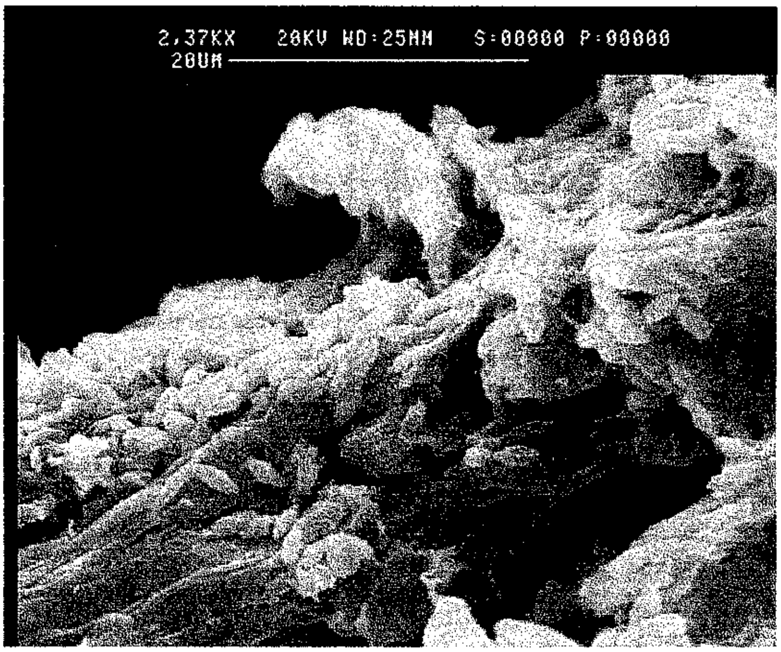

Fig. 13. Typical SEM micrograph of sawdust of *Pinus sylvestris* after loading with synthetic metallic nitrate solution of lead and cadmium.

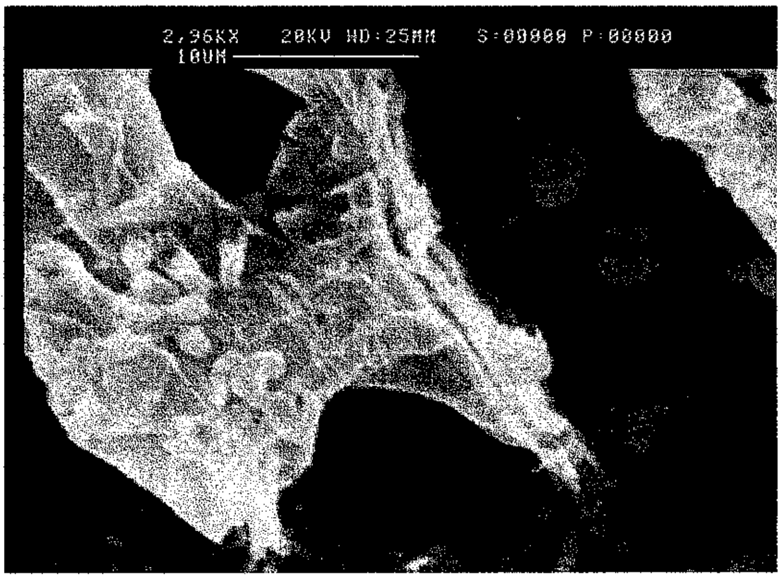

Fig. 14. Typical SEM micrograph of sawdust of *Pinus sylvestris* after loading with synthetic metallic nitrate of lead and cadmium.

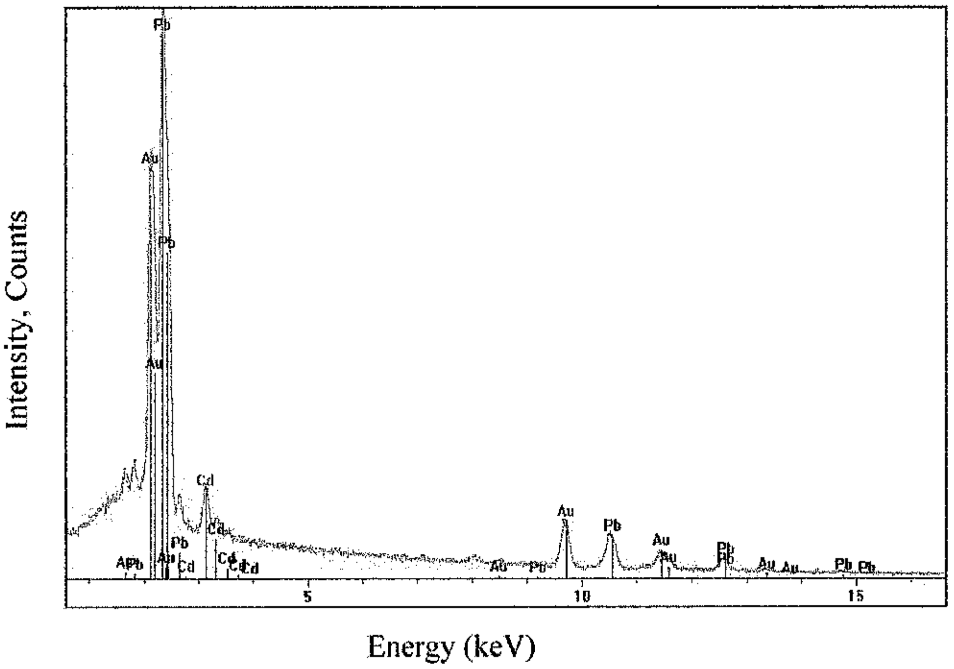

Fig. 15. Corresponding EDAX spectrum of loaded of sawdust of *Pinus sylvestris* after loading with synthetic metallic nitrate of lead and cadmium.

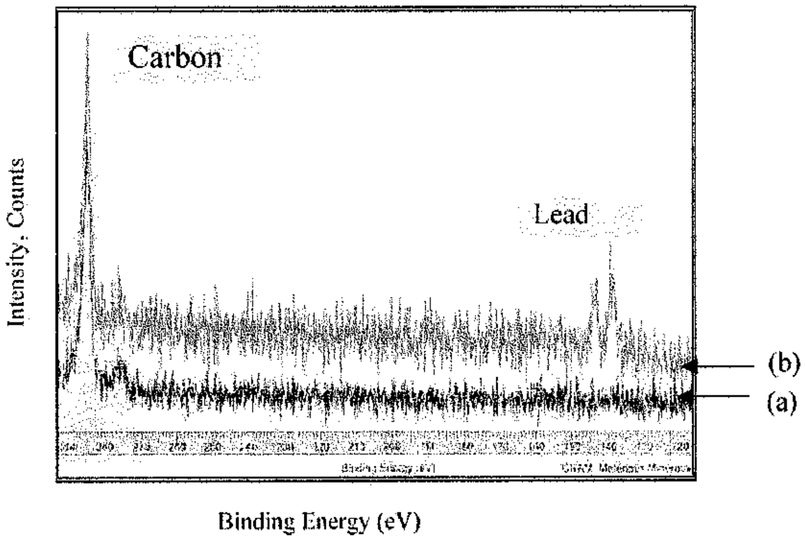

Fig. 16. XPS analysis spectra of *Pinus sylvestris* biomass: (a) before and (b) after lead uptake.

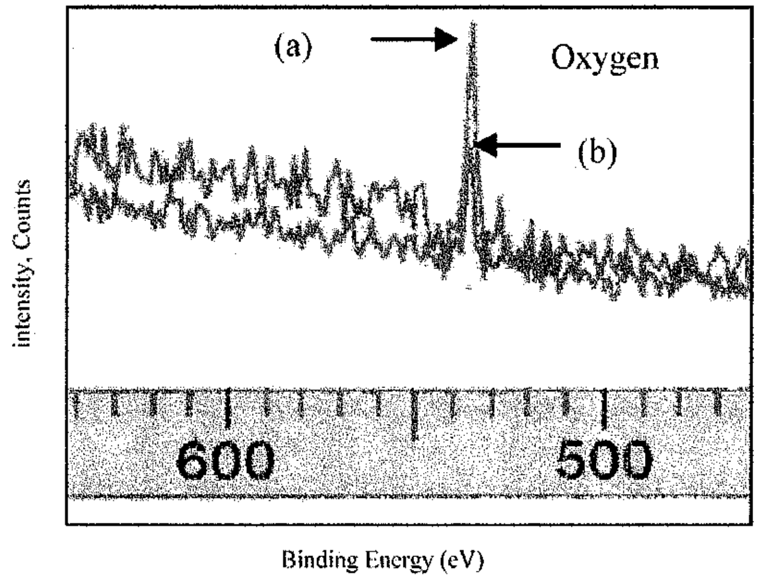

Fig. 17. High resolution oxygen XPS spectra of *Pinus sylvestris* biomass (a) before and (b) after lead uptake.

(Fig. 17). The atomic concentration of oxygen after lead biosorption decreases. Hence, lead biosorption is accompanied by a change in oxygen binding, providing evidence that the oxygen of carboxylic group takes part in lead biosorption. The oxygen peak was shifted by 0.73 eV after lead biosorption (Fig. 17). This shift could have been expected since $Pb(OH)_2$ pellets cover the sawdust surface (Figs. 13 and 14), it suggests that the oxygen of lignines reacts with the metallic ions. Similar results were reported by Kuyucak and Volesky [38].

4. Conclusion

The present study clearly establishes that sawdust of *P. sylvestris* is an effective adsorbent for Pb(II) and Cd(II) removal from aqueous solutions. The results obtained show that the sorption of lead is higher than that of cadmium. Moreover, both sorption capacity and sorption rate are strongly dependent on the initial concentration in heavy metals, initial pH of solution, and sawdust concentration.

Adsorption equilibrium can be simulated by Langmuir isotherms. These isotherms are influenced by the pH of initial metal ions concentrations as adsorption is essentially a phenomenon of surface.

The kinetics of sorption can be described by a model of a pseudo-second-order because of the strong correlation of the experimental results obtained with Ho and McKay's linearization. Two models of transfer were examined: external diffusion and intraparticular diffusion. The experimental data show that intraparticular diffusion is significant in the determination of the sorption rate. However, external diffusion has only a weak effect, all the weaker as stirring velocity hardly influences equilibrium in the stirring field explored.

It can be concluded that the use of *P. sylvestris* sawdust as an adsorbent may be an alternative to more costly materials such as activated carbon for the treatment of liquid wastes containing metal ions. Moreover, the rapid uptake allows to consider carrying out the sorption of heavy metals on column filled with this sawdust because the contact time between the metal solution and the adsorbent is generally short in this process. These results were confirmed working with some industrial sewage and the development on a pilot scale is now being studied.

Acknowledgements

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Sulphuric Acid

A molecule of **Sulphuric Acid, H2SO4,** consists of two atoms of hydrogen, one atom of sulphur and four atoms of oxygen

Sulphuric acid is a colourless viscous corrosive oily liquid, which has

- Melting Point : 10.3 degC
- Boiling Point : 338 degC
- Formula weight 98.08
- Specific gravity or density 1.94
- Flash point none

Sulphuric acid is the strong acid produced by dissolving sulphur trioxide in water.

```
SO3      +      H2O      ==>     H2SO4
```

The Strength of Acids is determined by the degree to which they are ionised in aqueous solution. For example, Sulphuric Acid, H2SO4, which is a strong acid is fully dissociated, and all the displaceable hydrogen in the acid is present in solution as Hydrogen Ion, H(+).

```
H2SO4           ==>    H(+)    +    SO4
              100% as H(+)
```

In contrast, the weak acids ethanoic acid, CH3COOH, is partially ionised in solution, and only approximately 5% of the displaceable Hydrogen in the acid is present in solution as hydrogen ion, H(+).

```
CH3COOH    ==>    H(+)    +    CH3COO(-)
                5% as H(+)
```

Properties of Sulphuric Acid

- Sulphuric acid is a powerful protonating agent.
- It is also a moderately strong <u>oxidizing agent</u>.
- Sulphuric acid is also a powerful <u>dehydrating agent</u> and is used to remove a molecule of water from many organic compounds.
- In dilute solution, sulphuric acid is a strong dibasic acid forming two series of salts.

A <u>Dibasic Acid</u> has two acidic hydrogen atoms in its molecules which can be ionised. Sulphuric Acid, H2SO4, is a dibasic acid, because it contains two hydrogens atoms which ionise in aqueous solution to become Hydrogen Ions, H(+).

```
H2SO4     ==>    2 H(+)     +    SO4(2 -)
```

Sulphuric acid is an important industrial chemical and it has many uses as a strong oxidising agent and a powerful dehydrating agent.

Commercially available sulphuric acid is as a 96-98% solution of the acid in water.

It is a powerful protonating agent.

It is also a powerful dehydrating agent and is used to remove a molecule of Water, HO_2, from many organic compounds.

The Dehydration Reactions of Alcohols results in their converted into an alkene, and involves the elimination of a molecule of water. Dehydration requires the presence of an acid and the application of heat.

Preparation of Sulphuric Acid

Combustion of Sulphur

When a small amount of Sulphur, S, is kindled on a deflagrating spoon, it burns with a bright blue flame when introduced into a gas jar containing Oxygen, O_2. A gas, Sulphur Dioxide, SO_2, is the main product of the combustion. However, a little Sulphur Trioxide, SO_3, is also formed, which makes the gas slightly cloudy.

$$S + O_2 \Longrightarrow SO_2$$

Sulphur Dioxide

$$2S + 3O_2 \Longrightarrow 2SO_3$$

Sulphur Trioxide

When shaken with water, the products of combustion dissolve, forming an acidic solution which turns litmus red.

$$SO_2 + H_2O \Longrightarrow H_2SO_3$$

Sulphur Dioxide — Sulphurous Acid

$$SO_2 + H_2O \Longrightarrow H_2SO_4$$

Sulphur Trioxide — Sulphuric Acid

Manufacture of Sulphuric Acid

Sulphuric acid was manufactured by the lead-chamber process until the mid-1930s, but this process has now been replaced by the contact process, involving the catalytic oxidation of sulphur dioxide.

Properties of Sulphuric Acid

The Contact Process is used for manufacturing sulphuric acid and fuming sulphuric acid from sulphur dioxide, which is made by burning sulphur or by roasting sulphide ores and oxygen (in the form of air) which combine to form sulphur trioxide in the presence of a catalyst. The reaction is exothermic and the conditions are controlled to keep the temperature at 450 degC. The catalyst used is valadium oxide (V_2O_5). The sulphur trioxide is dissolved in sulphuric acid to form fuming sulphuric acid, this is called oleum.

$$S(s) + O_2(g) \Longrightarrow SO_2(g)$$

Sulphur Dioxide

$$2SO_2(g) + O_2(g) \Longrightarrow 2SO_3(g)$$

Sulphu Trioxide

$$SO_3(g) + H_2SO_4(l) \Longrightarrow H_2S_2O_7(l)$$

Oleum

This Oleum, $H_2S_2O_7$, is then diluted with Water, H_2O, to produce concentrated Sulphuric Acid, H_2SO_4.

$$\underset{\text{Oleum}}{H_2S_2O_7(l)} + H_2O\ (l) \Longrightarrow \underset{\text{Sulphuric Acid}}{2\ H_2SO_4(l)}$$

Reactions of Sulphuric acid

Electrolysis of a Solution of dilute Sulphuric Acid

The Electrolysis of an Aqueous Solution of dilute Sulphuric Acid is often carried out in a Hofmann Voltammeter, an apparatus in which the gases evolved at the anode and cathode can be collected in separate graduated tubes. When the solution is electrolyzed hydrogen is produced at the cathode and oxygen at the anode. These gases can be shown to be present in a 2 to 1 ratio and result from the electrolysis of water under acidic conditions.

Sulphuric acid is a strong electrolyte is fully dissociated in aqueous solution.

$$H_2SO_4 \Longrightarrow 2\ H(+) + SO_4(2\ -)$$

Water is a weak electrolyte and is only slightly dissociated

$$H_2O \Longrightarrow H(+) + OH(-)$$

During electrolysis, the Hydrogen Ions, $H(+)$, migrates towards the cathode, and are discharged there (i.e. they gain an electron and are converted to hydrogen gas).

$$2\ H(+) + 2\ e(-) \Longrightarrow H_2-$$

At the anode the concentration of Hydroxyl Ions, $HO(-)$,is too low to maintain a reaction and the Sulphate Ions, $SO_4(2\ -)$ are not oxidized but remain on in solution at the end. Water molecules must be the species reacting at the anode.

$$2\ H_2O \Longrightarrow O_2 + 4\ H(+) + 4\ e(-)$$

The overall reaction is

Cathode Reaction :

2 H(+) + 2e(-) ==> H2
4 H(+) + 4e(-) ==> 2H2

Anode Reaction :

2 H2O ==> O2 + 4 H(+) + 4 e(-)

Overall Cell Reaction:

4 H(+) + 2 H2O ==> 2 H2 + O2 + 4 H(+)

For every Hydrogen Ions, H(+), discharged at the anode, another hydrogen ion is formed at the cathode. The net result is that the concentration of the Sulphuric Acid, H2SO4, remains constant and this electrolysis consists of the decomposition of water with the overall reaction

2H2O ==> 2H2~ + O2-

Ferrous Sulphate, Fe(II)SO4, is the salt formed when Iron, Fe, is dissolved in Sulphuric Acid, H2SO4.

Hydrogen Chloride, HCl, may be prepared in the laboratory by heating Concentrated Sulphuric Acid, H2SO4, with Sodium Chloride, NaCl.

NaCl + H2SO4 ==> NaHSO4 + HCl

Many Metallic Chlorides liberate Chlorine, Cl2, when treated with Sulphuric Acid, H2SO4, and Manganese Dioxide, MnO2).

Many Metallic Chlorides liberate Hydrogen Chloride gas, HCl, when warmed with concentrated Sulphuric Acid, H2SO4.

Sulphur Trioxide, SO3, is prepared by heating concentrated Sulphuric Acid, H2SO4, with a large excess of Phosphorus Pentoxide, P2O5.

H2SO4 + P2O5 ==> SO3 + 2 HPO3

Sulphur Dioxide, SO2, is usually made in the laboratory by heating concentrated Sulphuric Acid, H2SO4, with Copper turnings, Cu.

Cu + 2 H2SO4 ==> CuSO4 + SO2 + 2 H2O

Hydrogen Fluoride, HF, can be prepared in the laboratory by heating Concentrated Sulphuric Acid, H2SO4, with Calcium Fluoride, CaF2.

$$H_2SO_4 + CaF_2 \Rightarrow 2\,HF + CaSO_4$$

Hydrogen Iodide, HI, can be prepared by direct combination of the elements using a platinum catalyst. In the laboratory it is prepared by heating Concentrated Sulphuric Acid, H_2SO_4, with Sodium Iodide, NaI.

$$H_2SO_4 + 2\,NaI \Rightarrow 2\,HI + Na_2SO_4$$

Methanol, CH_3OH, does not undergo dehydration reactions. Instead, in reaction with Sulphuric Acid, H_2SO_4, the ester, Dimethyl Sulphate, $(CH_3)_2SO_4$, is formed.

$$\underset{\text{Methanol}}{2CH_3OH} \xRightarrow{\substack{\text{concentrated}\\ H_2SO_4}} \underset{\substack{\text{Dimethyl}\\ \text{Sulphate}}}{(CH_3)_2SO_4} + \underset{\text{Water}}{H_2O}$$

Sulphuric Acid, H_2SO_4, absorbs Ethylene, C_2H_4, at room temperature to form Ethyl Hydrogen Sulphate, $C_2H_5.HSO_4$, with much evolution of heat.

$$C_2H_4 + H_2SO_4 \Rightarrow C_2H_5.HSO_4$$

If this is treated with Water, H_2O and warmed, Ethanol, C_2H_5OH, is formed.

$$C_2H_5.HSO_4 + H_2O \Rightarrow C_2H_5OH + H_2SO_4$$

Uses of Sulphuric Acid

The Daniell Cell, which is a primary voltaic cell having a positive electrode of Copper, Cu, and a negative electrode of Zinc Amalgam, Zn (in alloy with Hg), was invented by the British chemist John Daniel in 1836AD.

The Zinc Amalgam electrode is placed in an electrolyte of dilute Sulphuric Acid solution, H_2SO_4, or Zinc Sulphate solution, $ZnSO_4$, in a porous earthenware pot. This porous pot stands in a solution of Copper Sulphate, $CuSO_4$, in which the Copper electrode is immersed.

The Zinc electrode, Zn, acts as a source of electrons, which flow through an external wire which connects the two electrodes, while the Zinc Ions, Zn^{2+}, from the electrode go into solution.

Cathode reaction : $Zn \Rightarrow Zn^{++} + 2\,e^{-}$

On reaching the Copper Electrode, these electrons combine with Copper Ions, Cu^{2+}, in solution and the discharged copper ions are deposited on the copper electrode as Copper metal, Cu.

Anode reaction : $Cu^{++} + 2\,e^{-} \Rightarrow Cu$

An equation for the overall chemical process is obtained by adding together the two half-cell reactions in such a way that the electrons "cancel out".