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Biomass Adsorbent for Removal of Toxic Metal Ions From Electroplating Industry Wastewater

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1. Introduction

The contamination of water bodies by heavy metals has been the subject of many studies worldwide. Several alternatives have been proposed in order to minimize the harmful effects that the disposal of these metals can cause to the environment.

A major challenge for the electroplating industry is finding solutions that equate to positive environmental and economic aspects regarding the treatment of their effluent. The adsorption process has been widely studied in order to solve the problem of many industries regarding the disposal of their effluent. Systems such as ion exchange resins, electrochemical process, chemical precipitation and activated carbon have been widely used in the processes of waste water purification. Such processes could have reduced its costs from the use of alternative materials for low cost. This has led many industries worldwide to invest in research aimed at obtaining cheap and plentiful materials that may have the same or greater capacity to remove pollutants from water bodies.

The biosorption has been presented as a promising alternative to solve the problem of contamination by heavy metals with low environmental and economic impacts.

In this chapter we introduce biosorption e process of heavy metals and discuss the implications of the technologies used in the electroplating industry to remove its contaminants.

1.1 Biosorbents

Materials of natural origin are generally used in biosorption studies (such as seaweed, biological depuration plant sludge, agricultural and industrial wastes) are inexhaustible, low-cost and non-hazardous materials, which are specifically selective for different contaminants and easily disposed by incineration.

The biosorbent terms refers to material derived from microbial biomass, seaweed or plants that exhibit adsorptive properties. Biosorption is the accumulation of metals by biological

materials without active uptake. This process may include ion exchange, coordination, complexation, chelation, adsorption and microprecipitation (Duncan et al., 1994) This biomass must be subjected to pre-treatment to obtain a better operating performance in pollutant removal using adsorption method (Naja et al., 2010).

An interesting feature is that the biosorbents are widely found in nature and they have low cost. In some cases they are agriculture waste such as corn cob (Shen & Duvnjak, 2005), coconut shell (Sousa, 2007), orange pulp (Almeida, 2005), peat (Gupta et al 2009) and sawdust (Yasemin & Zaki, 2007)

1.2 Ions metal biosorption

The process is based on the interaction of ions at the interface biomass / aqueous medium. The sorbent can be either a particulate material as a compact material. The separation can be performed in packed columns, fluidized beds or in the form of discs to be used in the filtration process. This configuration allows for regeneration and reuse of the adsorbent and its proper disposal (Vargas et al, 1995). The discovery and development of the biosorption process has supported the basis for an new technology in this field. Several authors have been devoted to the study and applicability of this new kind of technology (White, 1995; Volesky, 1990).

Agricultural waste is one of the rich sources of low-cost adsorbents besides industrial by-product and natural material. Due to its abundant availability agricultural waste such as peanut husk, rice husk, coconut shell, wheat bran and sawdust offer little economic value and, moreover, create serious disposal problems (Igwe & Abia,2007).

Biosorption is the capability of active sites on the surface of biomaterials to bind and concentrate heavy metals from even the most dilute aqueous solutions. Biosorption can be used for the treatment of wastewater with low heavy metal concentration as an inexpensive, simple and effective alternative to conventional methods. The process of metal ion binding is comprised of many physico-chemical processes like ion exchange, complexation, microprecipitation, and electrostatic interactions. Biosorbents for the removal of metals mainly come under the following categories: bacteria, fungi, algae, industrial wastes, agricultural wastes and other polysaccharide materials. In general, all types of biomaterials have shown good biosorption capacities towards all types of metal ions (Febrianto et al., 2009)

The biosorption results from electrostatic interactions and/or of the formation of complexes between metal ions and functional groups present on the surface of biosorbent. So many studies have been conducted to assess the potential for removing heavy metals from various biological materials (Hayashi , 2001). We can cite the seaweeds and their derivatives (Luo et al, 2006), chitosan (Ngah et al, 2011), lignin (Guo et al, 2008), wide variety of bacteria and fungi (Watanabe et al, 2003), agricultural residues (Sousa, 2007), among others. According to Volesky, (1990) biosorbent must have certain physical characteristics (surface area, porosity, grain size etc.) to get good ability to adsorption and to be used in an adsorption process.

1.3 Adsorbent used for removing pollutants

Adsorption process is essentially a surface phenomenon. Adsorbent having a good adsorptive capacity implies that it should present a large specific surface area. The adsorptive properties depend on the distribution of size pore and the nature of the solid surface. The adsorbents

most commonly used on an industrial scale are the activated carbon, silica gel, activated alumina and molecular sieves (Lopez & Gutarra, 2000) (Yasemin & Zaki, 2007). There is no doubt that the charcoal has become the most widely used solid, worldwide, as an adsorbent to remove pollutants in wastewater. According to its own characteristics, such as high porosity, chemical structure and high surface area, the activated carbon has an excellent ability to remove substances on its surface (Babel & Kurniawan, 2003). Added to this, the chemical structure of this material allows surface modifications by chemical or physical treatments, allowing an increase in adsorption capacity of this material.

On the other hand, it is also widespread agreement that even with all these features, the charcoal has some serious drawbacks to adsorptive processes. Some of them should be, for example, the fact that this material is not selective, and its market value is relatively high. Also, the reactivation of this material is not an easy process; cleaning the surface for subsequent applications is a one very expensive process. Moreover, the methods of recovery of coal, both the heat treatment as the use of chemicals, cannot regenerate the material with the same initial characteristics, leading to losses in their adsorption capacity. For these reasons, special attention has been focused on several other adsorbent materials. In particular, some natural materials, such as polysaccharides, clays, biomass, etc., that can remove pollutants from contaminated water at low cost of procurement has been widely researched around the world (Kumar, 2000; Crini, 2005, Crini, 2006). In fact, the cost of obtaining and regenerative capacity of such solid materials are important parameters when compared adsorbents materials.

№	pH	Adsorbent	Metal	Adsorption capacity $q_m(mg.g^{-1})$	Reference
1	-	Pomelo peel	Cd(II)	21.83	(Saikaew et al, 2009)
2	6	Acid-treated coconut shell carbon	Zn(II)	60.41	(Amuda et al, 2007)
3	5	Caladium bicolor	Cd(II)	42.19	(Jnr et al, 2005)
4	-	H_3PO_4 reated rice bran	Ni(II)	102	(Zafar et al, 2007)
5	6.6-6.8	Rice husk modified	Cd(II)	20.24	(Kumar and Bandyopadhyay, 2006)
6	5.3	Gelidium	Zn(II) Cr(III)	13 18	(Vilar et al, 2007)
7	5.3	Algal waste	Zn(II) Cr(III)	7.1 11.8	(Vilar et al, 2007)
8	5.0	Valonia tannin resin	Cu(II)	44.24	(Sengil et al, 2009)
9	5.5	Lignin	Cd(II)	25.4	(Guo, 2008)
10	5.3	Modified wood	Cu(II) Pb(II)	23.7 82.6	(Low et al, 2004)

Table 1. Maximum adsorption capacity of some adsorbent system given in literature

1.4 Modification of adsorbent

In general, raw lignocellulosic biosorbents were modified by various methods to increase their adsorption capacities because metal ion binding by lignocellulosic biosorbents is believed to take place through chemical functional groups such as carboxyl, amino, or phenolics. More recently, great effort has been contributed to develop new adsorbents and

improve existing adsorbents. Many investigators have studied the feasibility of using low-cost agro-based waste materials (Hashem, 2006; Hashem et al.,2006; Hashem et al. ,2006; Hashem et al., 2006; Hashem et al., 2006, Abdel-Halim et al., 2006; Hashem et al., 2006)

Agricultural by-products usually are composed of lignin and cellulose as major constituents and may also include other polar functional groups of lignin, which includes alcohols, aldehydes, ketones, carboxylic, phenolic and ether groups. These groups have the ability to some extent to bind heavy metals by donation of an electron pair from these groups to form complexes with the metal ions in solution (Pagnanelli, 2003).

In recent decades there has been a greater interest and concern about environmental issues. This has motivated the development of materials for low cost, wide availability and good adsorption capacity. At this particular point modification of adsorbent has been used in some cases with great success, with the purpose of increasing the adsorption capacity of these materials. Cellulose, hemicellulose and lignin are compounds that have structures with a large amount of hydroxyl groups. The availability of these groups are associated with good capacity to adsorb heavy metals such as Cu (II), Zn (II), Cd (II), Pb (II) among others. An interesting aspect is that these materials can be easily modified by introducing new functional groups.The modification reactions often employ a bioadsorbente polymerization reactions (Anirudhan & Noeline, 2005), functionalization with carboxylic groups, amines, amides (Shiba & Anirudhan, 2005) among others.

1.5 Electroplating wastewater

The industry of metal finishing and electroplating units are one of the major sources of pollutants which contribute greatly to the pollution load of the receiving water bodies and therefore increase the environmental risks

The industry of metal finishing and electroplating are one of the majorsource of heavy metals (Zn, Cu, Cr, …) and cyanide (Monser & Adhoum, 2002, 2002, Low & Lee,1991.). in the world. With the development of electroplating, the quantity of the electroplating wastewater have increased so fast in the last years. The heavy metals must be removed from wastewaters before discharge, as they are considered persistent, bioaccumulative and toxic (Sankararamakrishnan et al., 2007; Gupta, 2008), causing a serious threat to public health.

Heavy metal pollution around plating factories has been associated with the expansion of the plating industry in developing countries (Morgan & Lee, 1997 and Brower et al., 1997). Wastewater from the plating factories is divided into two types, one from plating manufacturing process and from rinsing process. In developed countries, removal of heavy metals in wastewater is normally achieved by advanced technologies such as ion exchange resins, vacuum evaporation, crystallization, solvent extraction and membrane technologies (Regel-Rosocka, 2010, Agrawal & Sahu, 2009, Nagarale, 2006, Ulbricht,2006). However, in developing countries, these treatments cannot be applied because of technical levels and insufficient funds. Therefore, it is desired that simple and economic removal methods to be utilized in developing countries could be established. Although chemical precipitation and coagulation–flocculation have been widely used to treat electroplating wastewater, their drawbacks like excessive chemicals consumption, sludge production, and impossibility of directly reusing heavy metals are obvious. On the other hand, adsorption methods such as ion exchange and membrane separation are simple methods for the removal of heavy metals. However, there is a limit in the generality in developing countries because chelating

and ion-exchange resins are expensive. Certainly, the cost plays an important and crucial role for determining which one is to be applied. Therefore, it is worthwhile to develop economic adsorbents of heavy metals which can be generally utilized in developing countries. Consequently, in the last decades alternative adsorbents for the treatment of heavy metal contamination have been investigated.

Cyanide is capable of forming a complex with almost any metal and resulting metal complexes. They are classified according to the strength of the metal–cyanide bond through the pH at which dissociation happens. Depending on the type of metal, some simple cyanides can dissolve in water forming metal ions and cyanide ions (equation 1):
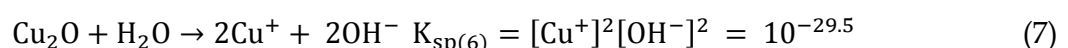
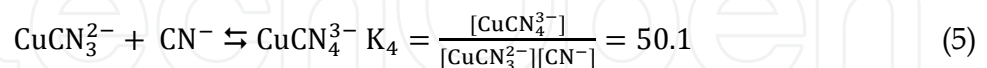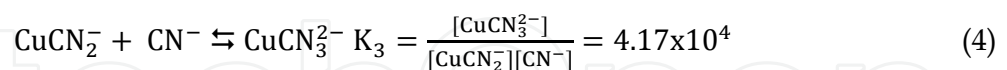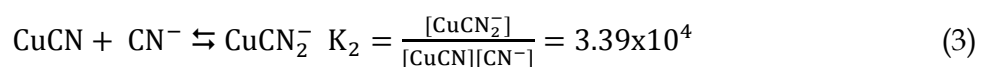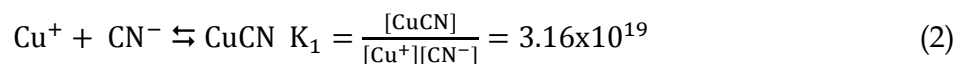$$M_y(CN)_x \leftrightarrows M_y^- + x(CN)^-$$ (1)

The solubility is influenced by pH and temperature (Botz et al., 1995) and the presence of other ligants as ammonia, for example (Franson, 1992).
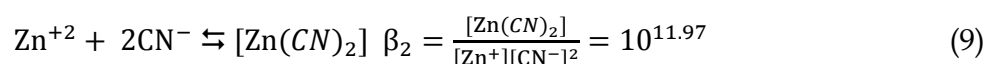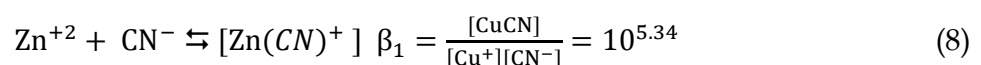
Cyanide complexes can generally be described by the formulae AyM(CNx), where A is an alkali or alkali-earth, y is the number of ions of A present, M is normally a transition metal, and x is the number of cyano-groups (Klenk et al., 1996).

Solution of metal ions, which already contain metal cyanide complexes, can replace the metal in the complex. The replacement depends on the respective formation constants. The metal ion in solution may also form a multimetal cyanide complex which may then precipitate as the complex, usually as an insoluble hydroxide or carbonate (Botz et al., 1995).
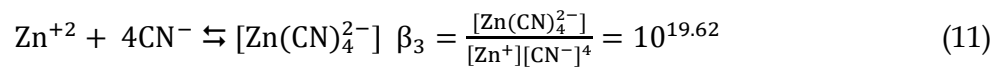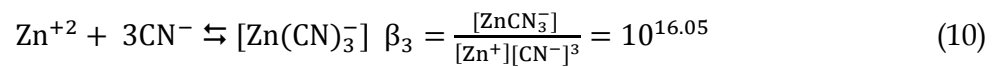
In the aqueous phase the equilibrium speciation of Cu(I) in cyanide solution can be represented by reactions (1)-(6) where K_1–K_4 are the equilibrium constants (here they are selected as 3.16×10^{19}, 3.39×10^4, 4.17×10^4 and 50.1, respectively (Lu et al., 2002).

$$Cu^+ + CN^- \leftrightarrows CuCN \quad K_1 = \frac{[CuCN]}{[Cu^+][CN^-]} = 3.16 \times 10^{19}$$ (2)

$$CuCN + CN^- \leftrightarrows CuCN_2^- \quad K_2 = \frac{[CuCN_2^-]}{[CuCN][CN^-]} = 3.39 \times 10^4$$ (3)

$$CuCN_2^- + CN^- \leftrightarrows CuCN_3^{2-} \quad K_3 = \frac{[CuCN_3^{2-}]}{[CuCN_2^-][CN^-]} = 4.17 \times 10^4$$ (4)

$$CuCN_3^{2-} + CN^- \leftrightarrows CuCN_4^{3-} \quad K_4 = \frac{[CuCN_4^{3-}]}{[CuCN_3^{2-}][CN^-]} = 50.1$$ (5)

$$CuCN \leftrightarrows Cu^+ + CN^- \quad K_{sp(5)} = [Cu^+][CN^-] = 10^{-20}$$ (6)

$$Cu_2O + H_2O \rightarrow 2Cu^+ + 2OH^- \quad K_{sp(6)} = [Cu^+]^2[OH^-]^2 = 10^{-29.5}$$ (7)

In the aqueous phase the equilibrium speciation of Zn(II) in cyanide solution can be represented by reactions (7)-(10) with the stability constant.

$$Zn^{+2} + CN^- \leftrightarrows [Zn(CN)^+] \quad \beta_1 = \frac{[CuCN]}{[Cu^+][CN^-]} = 10^{5.34}$$ (8)

$$Zn^{+2} + 2CN^- \leftrightarrows [Zn(CN)_2] \quad \beta_2 = \frac{[Zn(CN)_2]}{[Zn^+][CN^-]^2} = 10^{11.97}$$ (9)

$$Zn^{+2} + 3CN^- \leftrightarrows [Zn(CN)_3^-] \quad \beta_3 = \frac{[ZnCN_3^-]}{[Zn^+][CN^-]^3} = 10^{16.05} \qquad (10)$$

$$Zn^{+2} + 4CN^- \leftrightarrows [Zn(CN)_4^{2-}] \quad \beta_3 = \frac{[Zn(CN)_4^{2-}]}{[Zn^+][CN^-]^4} = 10^{19.62} \qquad (11)$$

The diagram of the Fig. 1 shows the speciation for the copper-cyanide-water system through the pH at which dissociation happens.

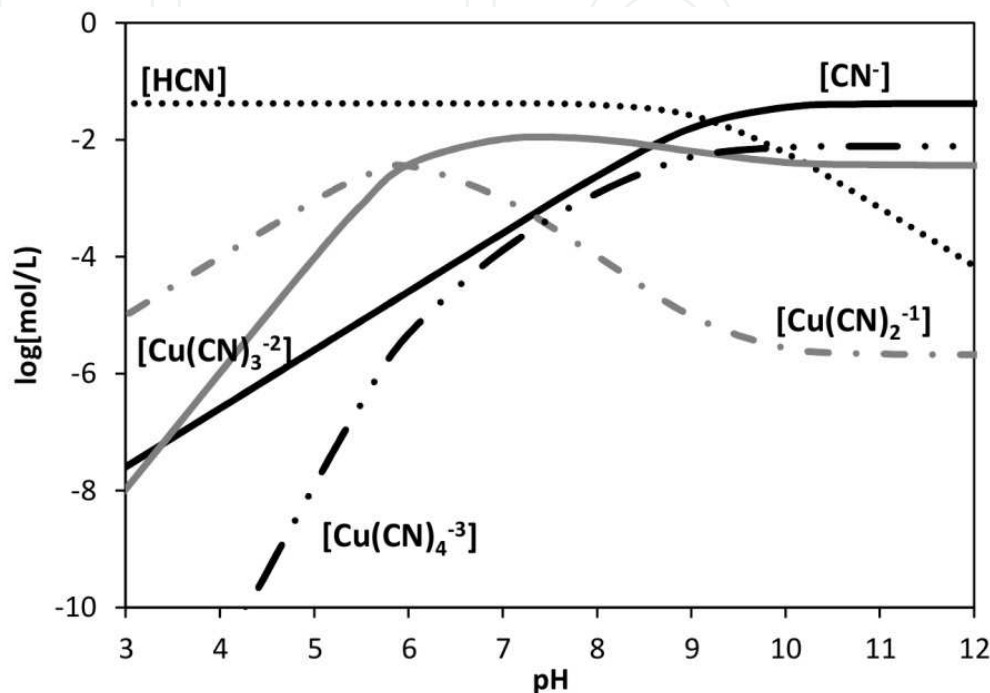Fig. 1. Speciation diagram for the copper-cyanide-water system to 25°C ;[Cu]=1.15x10^{-2}; [CN-]= 4.2x10^{-2} (K$_1$=3.16x10^{19}; K$_2$= 3.39x10^4; K$_3$ = 4.17x10^4; K$_4$= 50,1)

1.6 Metal cyanide complex on electroplating waterwaste

Cyanide, a poisonous substance dangerous to humans, animals, plants and aquatic organisms, can be found in the effluent of several industries such as paint and ink formulation, petroleum refining, explosives, case hardening, automobile industry, chemicals industry, pesticides industries, synthetic fiber production, electroplating, thermoelectric power stations, mining, electronics, and coke (Akcil, 2003; Clesceri *et al.*, 1998; Dash *et al.*, 2008; Monteagudo, 2004; Abou-Elela, 2008; Saarela et al., 2005; Dutra et al., 2008; Park *et al.*, 2008; Lanza & Bertazzoli, 2002; Han et al., 2005; Mudder & Botz, 2004; Yazıcı, 2007; Zvinowanda *et al.*, 2008; Fernando et al., 2008, Monser & Adhoum, 2002). Its effects on the human and the environment have been well reviewed by Mudder and Botz (2004). Due to its toxic nature, cyanide must be recovered, removed or destroyed.

The use of metals cyanide baths in the electroplating industry generates a strong concern related to environmental impacts due to high cadmium and cyanide toxicity (Smith and Mudder, 1991; Gijzen,2000; Waalkes, 2000). To minimize these environmental impacts wastewater treatment process are employed. The treatment intends to eliminate these toxic substances before their discharge in the environment (Butter e*t al.*, 1998). Several different cyanide removal technology are shown on table 2

Method	Description	Advantage	Disadvantage	Reference
Alkaline chlorination	Cyanide is oxidized to cyanate using chlorine or hypochlorite	Low cost when	These methods do not destroy the pollutants completely. Complete destruction of cyanate is difficult; It is less effective for iron cyanides; cannot recover cyanide; remaining chloramines and free chlorine lead to secondary contamination	(Freeman,1989; Han et al, 2005)
Hydrogen peroxide oxidation	Cyanide is oxidized to cyanate using hydrogen peroxide in the presence of copper ion	High Efficiency; Reactions involved in the process are very fast	Hydrogen peroxide is hazardous and expensive. Requires specialized equipment increasing the total capital cost. The treatment process generates ammonia, which is toxic to fish.	(Han et al, 2005)
Activated carbon adsorption	Cyanide is removed by activated carbon adsorption	Activated carbon performs both as an adsorbent and as a catalyst for the oxidation of cyanide. The adsorptive properties of activated carbons result from their high surface area and high degree of surface reactivity.	Regeneration of activated carbon is difficult	(Behnamfard & Salarirad,2009; Han et al, 2005)
Photochemical destruction	Cyanide is destroyed using ultraviolet (UV) irradiation	It ensures destruction of both free and some cyanide complexes, with weak-acid dissociable metals such as copper, without creating toxic residue	Usually inadequate by itself and requires chemical treatment, The wastewater must have a low concentration of organic matter	(Barakat et al, 2004;Han et al, 2005)
Ion exchange	Cyanide is removed by anion exchange resin	High selectivity of resins to metal cyanide complexes; Absence of hydrocyanic acid vapor which is hazardous to health.	Regeneration of resin is difficult since there are cyanide complexes besides free cyanides	(Kurama &.Çatalsarik, 2000; Han et al, 2005)
Gas-filled membranes	HCN transfer through a gas-filled hydrophobic microporous membranes to striping solution containing NaOH	Cyanide can be recovered. No secondary pollutants produced. Energy and chemical requirements are low. Simple operation	The membranes define the process costs	(Han et al, 2005)

| Chemical precipitation | It´s recommender ferrous sulfate addition to the cyanide-containing wastewater as a simple and efficient treatment process | Economic for small-scale operation; Easy to handle by unskillful labor. | Generates solid waste | (Ismail et al,2009) |

Table 2. Cyanide removal technology (Adapted from Han et al, 2005)

1.7 Technologies for the removal of cyanides

As cyanides are produced regularly by industries in large quantity in waste water streams, it is a potent health hazard for human and ecosystem. Cyanides can be removed from industrial wastes by biodegradation, physical and chemical methods (Patil and Paknikar, 2000; Ebbs, 2004). There are many reported processes for treating cyanide containing effluents (Monser & Adhoum, 2002; Dutra et al., 2008; Park et al., 2008; Mudder & Botz, 2004; Lanza & Bertazzoli, 2002; Han et al., 2005; Fernando et al., 2008; Yazıcı, 2007; Zvinowanda et al., 2008). These processes can involve biodegradation; adsorption on activated carbon; oxidation via chemical, electrochemical or photochemical processes (Monteagudo *et al.*, 2004; Saarela *et al.*, 2005; Dutra et al., 2008; Lanza & Bertazzoli, 2002; Yazıcı, 2007; Monser & Adhoum,2002); chemical precipitation (Park et al., 2008); hollow fiber gas membranes (Han et al, 2005); ultrasonic waves (Yazıcı, 2007); ion exchange (Fernando et al, 2008). The suitability of any of the above-mentioned processes to a specific cyanide-containing effluent depends on the effluent flow rate, cyanide concentration, associate chemical species, permissible level of cyanide in the effluent after treatment, technical level of the entity's employees and the economy and finances of the process.

2. Structural characterization of the biomass

There are several methods of elucidate the microstructure of the adsorbent materials from biomass. In this text, it will be present the most used by previous works in lignocellulosic biomass: Infrared spectroscopy (IR), X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). The macrocomponents which form the lignocellulosic fibers are cellulose, hemicellulose, lignin, pectin, wax and soluble substances, being the first three components responsible for the physical and mechanical proprieties of these fibers (Georgopoulos et al., 2005; Morán et al., 2008). This group includes wood agricultural crops, like jute, agricultural residues, such as sugar cane bagasse or corn stalks, banana fibers and other plant substances. Any lignocellulosic can be chemically modified (mercerization, acid treatment etc.) to enhance adsorption efficiency properties. This provides incentive for producing a variety of value-added products from different raw materials combined to provide improvements in cost or performance, or both (Gilbert, 1994).

2.1 Infrared spectroscopy

IR spectroscopy is a technique based on the vibrations of the atoms of a molecule. An infrared spectrum is commonly obtained by passing infrared radiation through a sample and determining what fraction of the incident radiation is absorbed at a particular energy. The goal of the basic infrared experiment is to determine changes in the intensity of a beam of infrared

pH	Technology	Pollutant	CN⁻ (mg.L⁻¹)	Efficiency (%)	Reference
10	Oxidation/Application of ferrate(VI)	Cyanide-copper-nickel system	26	98.96	(Seung-Mok & Tiwari, 2009)
10	Adsorption process/pistachio hull	Cyanide	100	99.00	(Moussavi &. Khosravi *et al*, 2010)
-	Adsorption process/Modified activated with carbon tetrabutyl ammonium (TBA)	Cyanide-copper-zinc system	40	73.00	(Monser &. Adhoum et al, 2002)
-	Adsorption process/Modified activated with carbon tetrabutyl ammonium (TBA)	Cyanide	40	52.5	(Monser &. Adhoum et al, 2002)
11	POA/TiO₂ and 200W(of UV irradiation)	Cyanide	26	99.40	(Barak et al, 2004)
10	Electrochemical processes	Cyanide-copper system	247	83.40	(Szpyrkowicz et al, 2000)
5.3	Integrated coagulation–gas-filled membrane absorption	Cyanide	1000-3500	> 98	(Shen et al, 2006)
9-11	Solvent extraction	Cyanide-copper system	1100	99	(Alonso-González et al, 2010)
3.2	Adsorption process	Cyanide	-	98	(Moussavi ,2011)
8.0	Chemical precipitation	Cyanide-zinc system	18	99.47	(Ismail *et* al,2009)

Table 3. Technologies for the removal of cyanides

radiation as a function of wavelength or frequency. The energy at which any peak in an absorption spectrum appears corresponds to the frequency of a vibration of a part of a sample molecule (Stuart, 2004). Thus, an infrared absorption spectrum of a material is obtained simply by allowing infrared radiation to pass through the sample and determining what fraction is absorbed at each frequency within some particular range (Bower & Maddams, 2006).

Some examples of IR spectra of the lignocellulosic material are shown in Fig. 1. These samples had been studied in previous works for removal of toxic metal ions from aqueous industrial effluents or as composite materials: Sugar cane bagasse (Sousa et al., 2009) and fibers: coir (Esmeraldo et al., 2010), sisal (Barreto et al., 2009), jute (Barreto et al., 2010a) and Banana (Barreto et al., 2010b). It can be observed that the components of biomass are most likely consisted of alkenes, esters, aromatics, ketenes and alcohol, with different oxygen-containing functional groups (Yang et al., 2007). The main lignocellulosic IR vibrational modes presented are from cellulose, hemicelluloses and lignin. All samples presented two main transmittance regions. The first one at low wavelengths in the range 1800-500cm⁻¹ and the second one at higher wavelengths corresponding to the 3700-2750cm⁻¹, approximately. However, there are modification in signal intensity of these spectra due to different cellulose, hemicelluloses and lignin concentrations of each material. A resume of the assignment of main IR bands in these materials was building with dates from literature (Esmeraldo et al., 2010; Barreto et. al., 2011, Barreto et al., 2010a; Barreto et al., 2010b,Yang et al., 2007; Viera et al., 2007; Morán et al., 2008; Bilba et al., 2007) and it is presents in Table 2.

The spectrum of the Fig. 2 exhibited O–H stretching absorption of around 3430 cm⁻¹, C–H stretching absorption of around 2920 cm⁻¹, C=C benzene stretching ring of around 1634 cm⁻¹

and C–O–C stretching absorption of around 1058 cm⁻¹. There are other bands with weak and very weak signal that are described in Table 4. These absorptions are characteristic of the common lignocellulosic fiber.
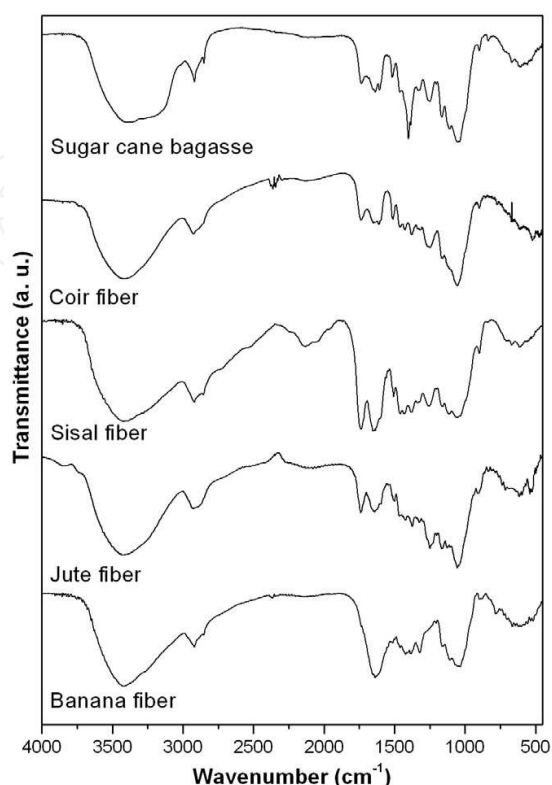

Fig. 2. Infrared spectra of natural lignocellulosic material.

Wavenumber (cm⁻¹)	Functional group
3600-3100	OH stretching
2970-2860	CH stretching of CH_2 and CH_3 groups
1765-1700	C=O stretching of acetyl or carboxylic acid
1634	Carbonyl stretching with aromatic ring
1620–1595	C=C stretching of aromatic ring (lignin)
1512	C=C stretching of aromatic ring (lignin)
1429	CH_2 bending
1376	C-H deformation
1335	OH in plane bending
1250	C-O stretching of ether linkage
1166	C-O-C antisymmetric bridge stretching
1062	C-O symmetric stretching of primary alcohol
904	β-Glucosidic linkages between the sugar units
900-700	C-H Aromatic hydrogen (lignin)
700-400	C-C stretching (lignin)

Table 4. Assignment of main functional groups of lignocellusosic materials.

The infrared spectroscopy was used to analyze the effect of the chemical treatment on the surface structure of the fiber. For example, Barreto and co-workers (Barreto et. al., 2011) observed that in sisal fibers, the weight loss due to the partial dissolution of hemicellulose,

lignin and pectin are clearly identified in the band in 1730 cm^{-1}, which disappears when the fibers are treated by a NaOH aqueous solution. This vibration mode was only observed to raw sisal fibers. Another important consideration is the broadness of the hydroxyl band at 3500–3300 cm^{-1}. For the natural sisal fibers the band is at 3419 cm^{-1}, characteristic of the axial vibration of hydroxyls from cellulose (carbons 2, 3 and 6 of the glucose) (Esmeraldo, 2006; Calado et. al., 2000) and it is showing a broadness as a function of the chemical treatment and due to changes of the inter- and intra-molecular hydrogen bonding in polysaccharides (Esmeraldo et al., 2010), which reaches a frequency of 3372 cm^{-1} for the fiber treated with NaOH 10%. However, for sugar cane bagasse study presents by Sousa and co-workers (Sousa et al., 2009), it was observed that acid treatment (1.0M HCl) removed or decreased some modes of lignin: absorptions due to C–H$_n$ (alkyl and aromatic) stretching vibrations (2918 and 2850 cm^{-1}), absorptions characteristic of the C=O stretching vibration (1708 cm^{-1}), and a signal typical of an aromatic skeleton (1604 cm^{-1}). It can also be noted that the intensities of almost all bands were lower after acid treatment. Thus, IR spectroscopy is an important tool to evaluate the changes modification of the biomass structure before and after to the chemical treatment.

2.2 X-ray diffraction

XRD is the most widely used technique for general crystalline material characterization. It is noncontact and nondestructive, which makes it ideal for in situ studies (Brundle et al., 1992). It is routinely possible to identify phases in polycrystalline bulk material and to determine their relative amounts from diffraction peak intensities. The XRD measurements are used to examining crystallite solid as ceramics, metals, geological materials, organics and polymers. The samples for measurements may be single crystals, powders, sheets, films and fibers.

Cellulose is the main renewable carbon source in nature. It presented a high organized state nature (fibrous crystal) due to its linear polymer arrange of pure anhydroglucose units connected by 1,4β-glucosidic bonds (Chang et al., 1981). Each residue is rotated 180° compared with its neighbors. The degree of polymerization (DP) of native cellulose is in the range of between 7,000 and 15,000, where DP = Molecular weight of cellulose /Molecular weight of one glucose unit. It occurs in crystal and noncrystal regions as well as in association with lignin deposition in the secondary wall. The cellulose chains are oriented in parallel and form highly organized crystalline domains interspersed by more disorganized, amorphous regions. Cellulose chains form numerous intra- and intermolecular hydrogen bonds, which account for the formation of rigid, insoluble microfibrils (Buckeridge et al., 2011). The native crystalline form has a structure designated as type I, which can be converted into type II by alkaline treatment. Fig. 3 shows a representative model of the
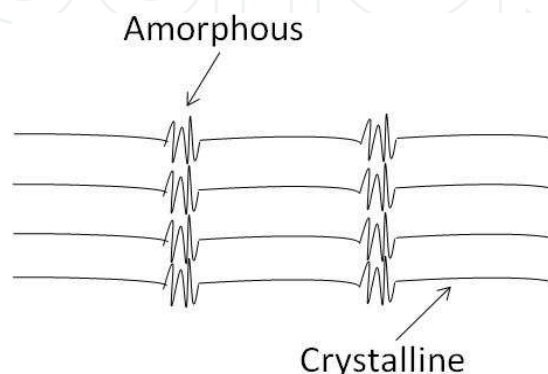

Fig. 3. Fibrillar model of cellulose.

molecular orientation in the crystallite. One can observed that there are intermittent highly ordered areas labeled crystalline regions, separates by less ordered or amorphous regions. This characteristic is important to understand the degradation mechanism of lignocellulosic material. For instance, amorphous regions of the cellulose are first hydrolyzed followed by hydrolysis of crystalline regions at a much slower rate.

Fig. 4 shows the XRD patterns of the untreated and acid treated sugar cane bagasse. Three peaks are presented in the directions of 15.2^0, 16.5^0 and 22.4^0. They assign the cellulose standard profile from JCPDS (Joint Committee on Powder Diffraction Standards, 1986). Ouajai and Shanks (Ouajai & Shanks, 2005) observed these same directions in hemp fiber and labeled them as 101, 10$\bar{1}$ and 002 diffraction planes from cellulose crystalline phase. Besides this phase, there was an amorphous phase characterized mainly as lignin. This polymer is associated to the cellular wall, conferring mechanical strength to the fiber, and when its concentration increases, the crystalline fraction decreases. The sugar cane bagasse fibers contain approximately 46% cellulose, 25% hemicelluloses and 21% lignin as the main components (Buckeridge et al., 2011). It also observed three other peaks on 26.52^0, 29.36^0 and 30.84^0 for both samples that could be attributed to impurities such as SiO_2 and $CaCO_3$, whose intensities decreased after acid treatment.
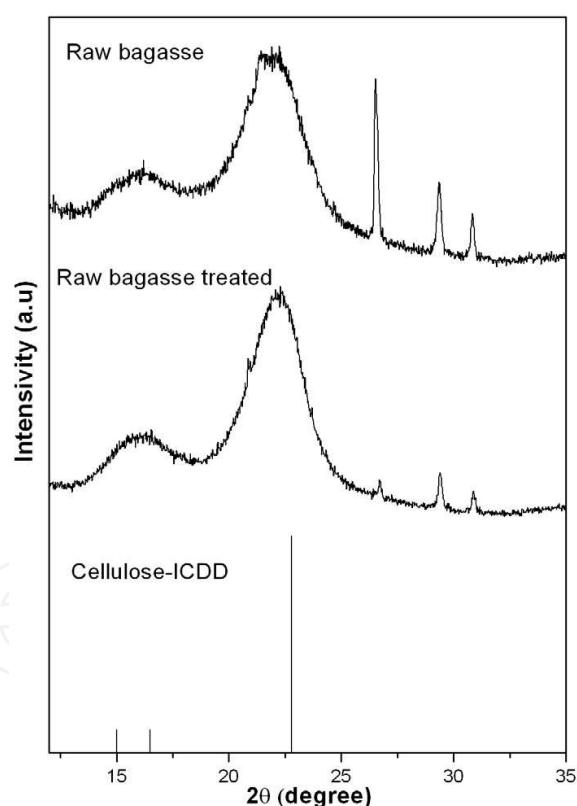

Fig. 4. XRD of the raw sugar cane bagasses and treated with 1.0M HCl, showing the crystalline and amorphous phases obtained by in comparison to data from ICDD.

The diffraction pattern from amorphous materials (including many polymers) is devoid of the sharp peaks characteristic of crystals and consists of broad features or halos. Many polymers, as biomass used to adsorbent material, are amorphous or semicrystalline, and for polymeric materials, XRD is used to clarify the structure, morphology, and degree of crystallinity. The

sugar cane bagasse crystalline fraction (F) can be obtained through separation and integration of crystalline and amorphous peaks areas under the diffraction X-rays plot, by the Equation (12):

$$F = \frac{\sum I_C}{\sum (I_C + I_A)} x 100 \tag{12}$$

where, I_C is the difractogram total crystalline phase area, and the I_A is the difractogram total amorphous phase area. For XRD presented in Fig. 3, the F value for the untreated material (62%) was close to the acid-treated material (67%) (Sousa et al., 2009). However, depend on biomass, the F value can present results in different ways. As it was observed for the banana fiber (Barreto et al., 2010b): the raw material presented 63.5% and after mercerization treatment (NaOH 0.5%), this value increased to 79.2%. This difference was due to the lignin be partially removed in alkaline solution, i. e., the banana fiber lost part of its amorphous component. Thus, the F values depend on the natural concentrations of lignin, cellulose and hemicelluloses presented by biomass and chemical treatment efficiency to remove amorphous phases.

2.3 Scanning electron microscopy

The SEM provides the investigator with a highly magnified image of the surface of a material that is very similar to what one would expect if one could actually "see" the surface visually (Brundle et al., 1992). SEM images the sample surface by scanning it with electron beams in a raster scan pattern. The electrons interact with the sample atoms producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity (Liu et al., 2010).

Not only is topographical information produced in the SEM, but information concerning the composition near surface regions of the material is provided as well. Additionally, the SEM can also be used to provide crystallographic information. Surfaces that to exhibit grain structure (fracture surfaces, etched, or decorated surfaces) can obviously be characterized as to grain size and shape. Thus, SEM can be used to materials characterization: topographical imaging, Energy-Dispersive X-Ray analysis and the use of backscattering measurements to determine the composition of the systems.

The surface morphology and porosity of natural fiber have been recognized as significant factors for composite interfaces, and their effects on the performance of composites have been investigated (Han & Choi, 2010). This information about is also important for an adsorbent. It is possible observe the grain or fiber size, porosity and morphology and compare to before and after some chemical treatment employed. The increase or decrease to adsorption capacity can be the answer in this way. Thus, surface morphology and microstructure of the adsorbents can be studied by SEM. For biomass, it is necessary coat the sample with a conductor material, as gold, platinum or with a layer of carbon. This happens due to slow electron conductivity of the kind of the material and this affects the images quality.

Fig. 5(a) shows the SEM morphology at raw banana fiber. It is observed a regular structure with discrete net fibrils due to the presence of hemicelluloses, lignin, and wax, where these constituents confer mechanical strength to the natural composite. After alkali treatment

(NaOH 1%), there is considerable structure modification as a visible separation of the fibrils, as are shown in Fig. 5(b). This happened due to remove partially of the some components. One of the aims of this treatment was to increase the surface area and decrease the hydrophilic groups. This hydrophilic nature can lead to incompatibility and poor wettability in a hydrophobic polymer matrix, and weak bonding in the fiber/matrix interface. Some cavities also appeared due to modifications on the surface.

(a)   (b)
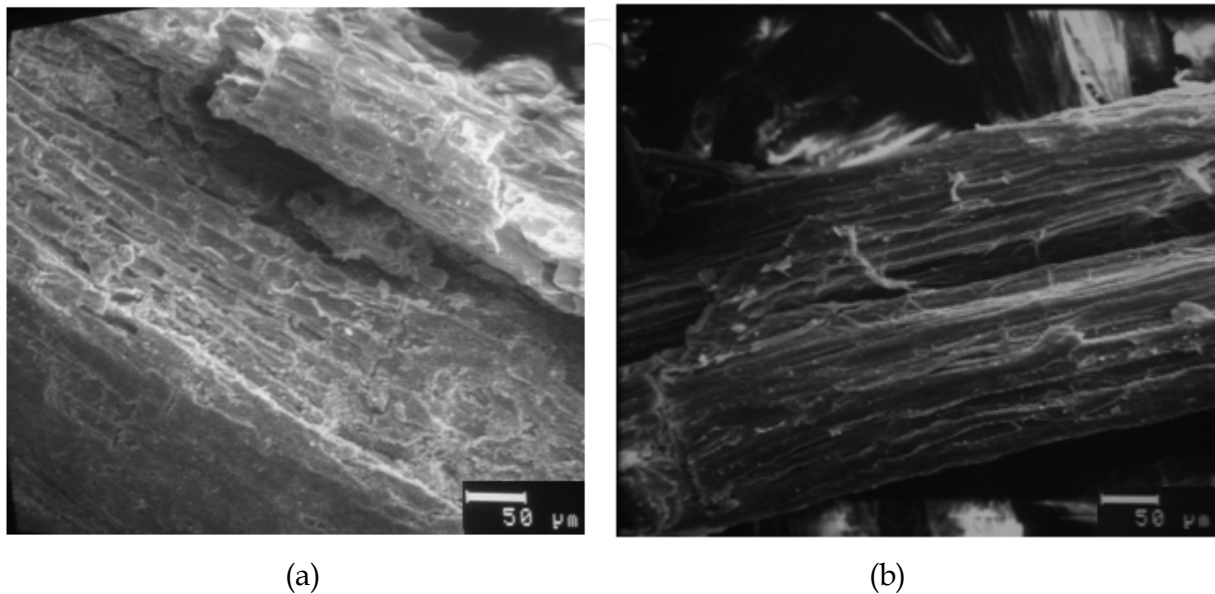
Fig. 5. SEM of the (a) raw banana fiber and (b) after alkali treatment with NaOH 1%

In other example, it is presented the raw sugar cane bagasse microstructure, see Fig. 6 (a). This material presents a reasonable homogeneity in aggregate shape. However, after acid treatment with HCl, some impurities were removed Fig. 6(b). It was also evidenced exposure and dispersion of the fibers, resulting in increased roughness. This procedure increases the superficial area of the sugar cane bagasse fiber and contributes to improve the metal adsorption capacity. Consequently, this fiber can be used as an efficient natural material to remove toxic metal ions from electroplating industry wastewater. A comparative study between metal adsorption behavior and lignocellulosic biomass morphology was

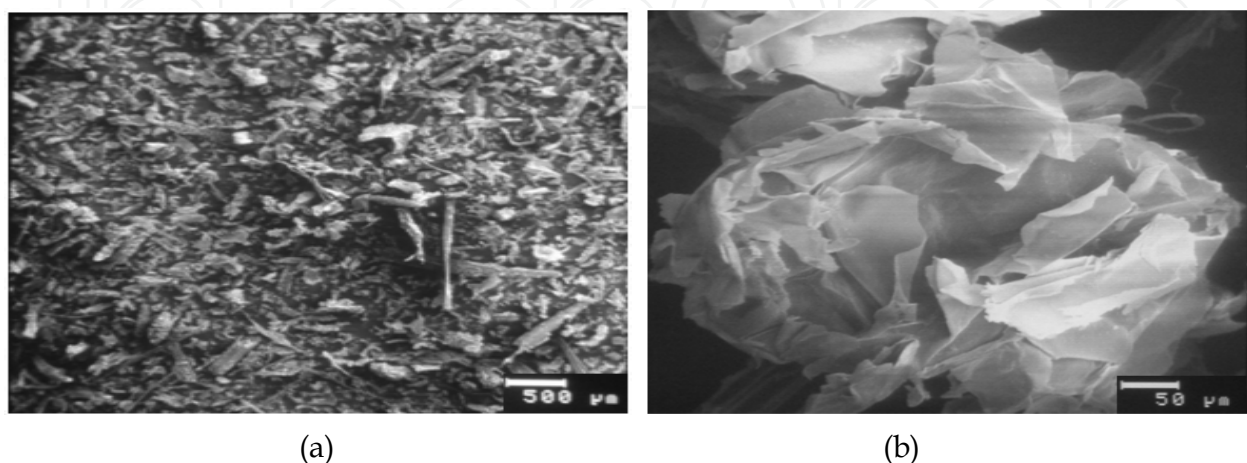(a)   (b)

Fig. 6. SEM of the raw sugar cane bagasse (a) and after acid treatment with HCl (b).

presented in previous studies (Bower & Maddams, 2006; Barreto et al., 2010b). The important observation is that biomass chemical modified was more efficient than raw material in the metal removal from aqueous solution. Additionally, this kind of material, when used to adsorption material, has the advantage of low density, low cost, recyclability and biodegradability.

3. Adsorption of single and multi-metal ions

3.1 Adsorption kinetics

The study of the time dependence of adsorption on solid surface (adsorption kinetic) help in predicting the progress of adsorption in industrial application, however the determination of the adsorption mechanism is also important for design purposes. In a solid-liquid adsorption process, the transfer of the adsorbate is controlled by either boundary layer diffusion (external mass transfer) or intra-particle diffusion (mass transfer through the pores), or by both (Dabrowski, 2001). It is generally accepted that the adsorption dynamics consists of three consecutive steps:

- Transport of adsorbate from the bulk solution to the external surface of the adsorbent by diffusion through the liquid boundary layer.
- Diffusion of the adsorbate from the external surface and into the pores of the adsorbent.
- Adsorption of the adsorbate on the active sites on the internal surface of the pores.

The last step, adsorption, is usually very rapid in comparison to the first two steps. Therefore, the overall rate of adsorption is controlled by either film or intra-particle diffusion, or a combination of both. Many studies have shown that the boundary layer diffusion is the rate controlling step in systems characterized by dilute concentrations of adsorbate, poor mixing, and small particle size of adsorbent (Singh & Mohan, 2004).

In order to investigate the adsorption kinetics of metal ions adsorption on adsorbent, pseudo-first order, pseudo-second order, and intraparticle diffusion models are the models more frequently applied, which are pseudo-first-order (Lagergren, 1898), pseudo-second-order (Ho & Mckay, 1999) and intraparticle diffusion model (Weber & Morris, 1963), expressed as:

$$\log(q_e - q_t) = \log q_e + \frac{K_1}{2.303} \times t \qquad (13)$$

$$\frac{t}{q_t} = \frac{1}{K_2 \, q_e^2} + \frac{1}{q_e} \times t \qquad (14)$$

$$q_t = k_{id} t^{1/2} + C \qquad (15)$$

Where, q_e and q_t are the adsorption capacities (mg g^{-1}) at the equilibrium and at a time determined, respectively, t the time, while K_1 (min^{-1}) and K_2 (mg g^{-1} min^{-1}) are rate constants related to the first order and second order models. C is the intercept and k_{id} is the intra-particle diffusion rate constant (mg g^{-1} min$^{-1/2}$), which can be evaluated from the slope of the linear plot of q_t versus $t^{1/2}$. The values C provide information about the thickness of the boundary layer, the larger the intercept, the greater the boundary layer effect (Kavitha & Namasivayam, 2007).

If intra-particle diffusion occurs, then q_t versus $t^{1/2}$ will be linear and if the plot passes through the origin, then the rate limiting process is only due to the intra-particle diffusion. Otherwise, some other mechanism along with intra-particle diffusion is also involved.

The typical results obtained by Sousa et al., 2010; Moreira et al., 2010 for the metal ions sorption onto lignocellusic adsorbents by investigating the pseudo first and pseudo-second-order rate equations order and intraparticle diffusion model are presented in Table 5. Applications of these rate equations for describing the kinetics studies were investigated for batch technique due its simplicity. For this, erlenmeyer flasks of 50mL containing 0.30 g of adsorbent with 10 mL of multi-metal solution (100 mg L⁻¹, at pH 5.0) were shaken (at 300 rpm) in room temperature, at 28°C. After a predetermined time, volumes of the solution were removed, filtrated and analyzed. The amount of adsorption was calculated at equilibrium achieved in 4-5 h by equation 16.

$$q_e = \frac{(C_o - C_e)V}{m}$$

(16)

Where: C_o is the solution initial concentration (mg L⁻¹); C_e is the equilibrium concentration of adsorbate (mg L⁻¹); V is the solution volume (L) and m is the mass do adsorbent (g).

The linear plot of log (q_e-q_t) versus t for pseudo first order, $1/q$ versus t for pseudo-second order and q versus $t^{1/2}$ for intraparticle diffusion models are used for constants K_1, K_2 and K_f calculated from slope of the corresponding linear equations and correlation coefficients (R^2). From results presented in Table 5 can be noted that the experimental q_e values show a reasonable agreement with the calculated q_{cal} value by first order equation, indicating that the adsorption system belongs to the first order reaction. In contrast, do not agree between experimental and calculated q_{cal} values by second-order equation is observed. This indicates that the adsorption of multi-metal on the sugar cane bagasse is not described by a second order reaction.

When the intraparticle diffusion model can be applied then the plots of q versus $t^{1/2}$ is linear, and if it passes thought the origin the limiting processes is only due to intraparticle diffusion (Weber & Morris, 1963). However, since that the plots of q versus $t^{1/2}$ (not showed) was linear but is not pass through origin, then the intraparticle diffusion is not the only rate limiting mechanism on multi-metal adsorption on the cane sugar bagasse studied.

Table 5 presented the results obtained of adsorption kinetics studies for Cu^{2+}- Ni^{2+} -Cd^{2+} on the sugar cane bagasse (Sousa et al.,2010). It is observed that the experimental q_e values are reasonable in agreement with the calculated q_c value for first order equation, indicating that the adsorption system belongs to the first order reaction. In contrast, do not agree between experimental and calculated q_e values by second-order equation can be observed. This suggest that adsorption of Cu^{2+}- Ni^{2+} - Cd^{2+} on the sugar cane bagasse not follows a second order reaction. However, the results found by Moreira et al., 2010 showed that Cu^{2+}, Ni^{2+} and Cd^{2+} adsorption on cashew bagasse has a good agreement between the experimental (q_e) and the calculated (q_{ca}) values, as shown in Table 5. The high values for coefficient of correlation, R^2, indicate that there is strong evidence that the Cu^{2+}, Ni^{2+} and Cd^{2+} adsorption onto cashew bagasse follows the pseudo- first and second order kinetic models.

When the intraparticle diffusion model can be applied then the plots of q versus $t^{1/2}$ is linear, and if it passes thought the origin the limiting processes is only due to intraparticle diffusion

(Weber & Moris, 1963). However, since that the plots of q versus $t^{1/2}$ (not showed) was linear but is not pass through origin, then the intraparticle diffusion is not the only rate limiting mechanism on multi-metal adsorption on the cane sugar and cashew bagasse studied. The values correlation coefficient (R^2) obtained for the plots were not satisfactory.

Metal	C_o (mg L^{-1})	$q_{e(exp)}$ (mg g-1)	$q_{(cal)}$ (mg g^{-1})	K_1 (min^{-1})	R^2	$q_{(cal)}$ (mg g^{-1})	K_2 (mg g^{-1} min^{-1})	R^2	K_f (mg g^{-1} min$^{-1/2}$)	R^2
			First order				Second order		Intraparticle Diffusion	
			sugar cane bagasse							
Cu^{2+}	74.14	2.015	2.01	0.98	0.890	3.11	0.140	0.88	0.79	0.860
Ni^{2+}	108.81	0.827	1.05	0.61	0.890	-	-	-	0.29	0.810
Cd^{2+}	117.99	2.54	2.56	0.51	0.920	5.44	0.040	0.93	0.51	0.860
			Cashew bagasse							
Cu^{2+}	102.18	1.982	1.933	0.016	0.956	1.95	0.518	1.00	0.009	0.779
Ni^{2+}	82.93	1.588	1.573	0.006	0.790	1.59	0.873	1.00	0.003	0.755
Cd^{2+}	90.70	1.803	1.800	0.012	0.852	1.80	0.022	1.00	0.001	0.909

Table 5. Parameter of adsorption kinetic in the sugar cane bagasse and cashew bagasse in multi-metal solutions (10-200 mg.L^{-1}) at pH 5.0 , time equilibrium achieved in 4-5 h.

3.2 Adsorption isotherm equilibrium

Most experimental and theoretical studies of the adsorption at solid-liquid interface have been carried for single or multi metal ions removal from aqueous solution by diverse types of low cost adsorbents (Pasavant et al., 2006; Aksu et al.,2002; Cay et al., 2004; Amarasinghe & Williams, 2007). In the practice, the adsorption metal ions from wastewater generally involve the simultaneous presence of metal ions in wastewater promoting a competition between different metal ions by adsorption site. However, study of equilibrium modeling of multi-metal ions is essential for understand the real system, but usually are neglected (Febrianto, 2009).

Adsorption is an important process that describes the interaction between adsorbent and metal ion to develop design model for wastewater industrial treatment. The applicability of relationship between the experimental adsorption capacities and the metal ions concentrations (adsorption isotherm) have been widely used by the Langmuir and Freundlich models (Frebianto et al., 2009).

3.2.1 Langmuir model

The Langmuir adsorption model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, with no lateral interaction between the adsorbed metal. The Langmuir adsorption isotherm model is successfully used to explain the metal ions adsorption from aqueous solutions (Langmuir, 1918). The expression of the Langmuir model is given by Eq.(17),

$$q_e = \frac{q_{max}.K_L.C_e}{(1 + K_L C_e)} \tag{17}$$

and the linearized Lagmuir isotherm equation can be expressed as:

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \left(\frac{1}{q_{max}K_L}\right)\left(\frac{1}{C_e}\right) \tag{18}$$

3.2.2 Freundlich model

The Freundlich isotherm gives the relationship between equilibrium liquid and solid phase capacity based on the multilayer adsorption (heterogeneous surface). This isotherm is derived from the assumption that the adsorption sites are distributed exponentially with respect to the heat of adsorption and is given by Freundlich, 1906).

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. The Freundlich equation is expressed as:

$$q_e = K_F C_e^{1/n} \tag{19}$$

and linearized Freundlich isotherm equation can be expressed as:

$$\log q_e = \log K_F + 1/n \log C_e \tag{20}$$

Where q_e (mg.g^{-1}) is the amount of metal ion adsorbed, expressed as mg metal ions per g adsorbent, C_e (mg.mL^{-1}) the equilibrium concentration of metal ion in solution, q_{max} (mg.g^{-1}) and K_L (L.mg^{-1}) are constants of Langmuir related to the maximum adsorption capacity (mg.g^{-1}) and heat of adsorption, respectively, while K_F (mg$^{1-(1/n)}$.(g^{-1}).L$^{1/n}$) and $1/n$ are constants of Freundlich related to the adsorption capacity and to surface heterogeneity, respectively.

3.2.3 Applications of Langmuir and Freundlich models

The linear fit of the experimental data using the Langmuir and Freundlich models permitted to obtain correlation coefficients greater than 0.90. Although its satisfactory value indicate, the applicability of both models is very difficult to identify the adsorption equilibrium model which represented the experimental data most correctly considering only the correlation coefficients. Hence, a parameter known as normalized percent deviation, P, (Ayranci, 2005) can be applied, according to the following equation 21:

$$P = (100/N) \sum \left(|q_e - q_{cal}|/q_e\right) \tag{21}$$

where q_e is the experimental adsorption capacity, q_{cal} the predicted adsorption capacity, and N the number of observations. The lower the P value is, better the fit is.

According to the literature (Cooney, 1993), the slope of the initial curvature of an adsorption isotherm indicates whether or not an adsorption system is efficient, which, for a Langmuir isotherm, can be expressed in terms of the separation factor R_L (Cooney, 1993; Ngah et al, 2008):

$$R_L = 1/(1 + K_L C_o) \tag{22}$$

where K_L (L mg^{-1}) is the Langmuir constant and C_o the metal ion initial concentration.

The type of isotherm is considered to be unfavorable, i.e., the solute has a preference for adsorption to the solid phase over dissolution in the liquid phase ($R_L > 1$), linear ($R_L=1$), favorable ($0 < R_L < 1$) or irreversible ($R_L=0$) depending on the value of R_L (Cooney, 1993, Ngah et al, 2008). The experimental R_L values were between 0 and 1 for all initial concentrations as known in Tables 6 and 7, hence, adsorption of metals ions studied on the adsorbent is considered to be favorable.

Applications of Langmuir and Freundlich models for describing adsorption isotherms with green coconut shell powder and cane sugar bagasse (treated with sodium hydroxide) for toxic metals removal from aqueous effluents were studied (Sousa et al., 2011; Sousa et al., 2010). Equilibrium adsorption isotherms of multi-metal (Cd^{+2}-Cu^{+2}-Ni^{+2}-Pb^{+2}-Zn^{+2}) on the green coconut shells and cane sugar bagasse are given in Fig. 7. The parameters of Langmuir (K_L; q_{max}) and Freundlich (K_F; $1/n$), determined from the slope and intercept of the plots of $1/q_e$ versus $1/C_e$ and log q_e versus log C_e are shown in Tables 6 and 7.
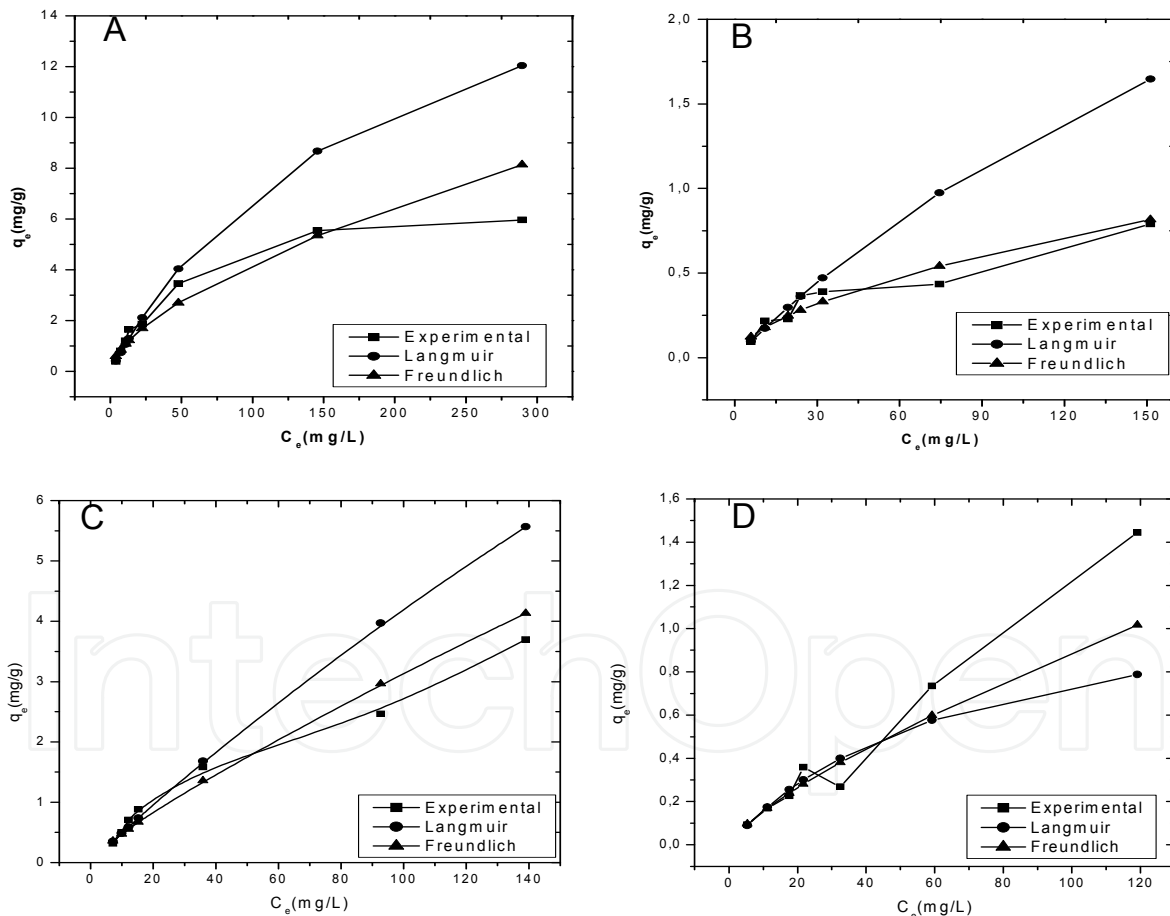

Fig. 7. Adsorption isotherm to metal ions: Pb^{+2}(a), Cd^{+2}(b), Cu^{+2}(c) and Ni^{+2}(d) on sugar cane bagasse, contact time 24h and pH 5.0.

The P values calculated in according to the Langmuir and Freundlich equations for single and multi-systems for sugar cane bagasse are given in Tables 6. It is observed that for single metal ion system the P deviations are lowest when the experimental data were fitted to the

Langmuir equation for all single metal ions studied, while the Freundlich model proved suitable for multi-metal system

The Langmuir and Freundlich isotherms for multi-metal ions adsorption on green coconut shell powder are shown in Fig. 8. The parameters determined for single and multi-metal ions each model are given in Table 3. The experimental data show that the Langmuir-type isotherms describe well the adsorption mechanism for Pb^{+2}, Ni^{+2} and Cd^{+2}, while Zn^{+2} and Cu^{+2} are of the Freundlich-type as can be observed by the values of correlation coefficients (R^2). The adsorption capacity of the multi-metals studied followed the order: $Zn^{+2} > Pb^{+2} > Cu^{+2} > Cd^{+2} > Ni^{+2}$. This can be attributed to the specificity of active sites, to varying affinities for adsorption or to competitive effects. Sekhar et al., 2003 referred that multicomponent systems, the complex interactions of several factors such as ionic charge and ionic radii will account for the differences in the metal removal capacity of the adsorbent. As a result, ordering of the metal ions based on a single factor is very difficult.
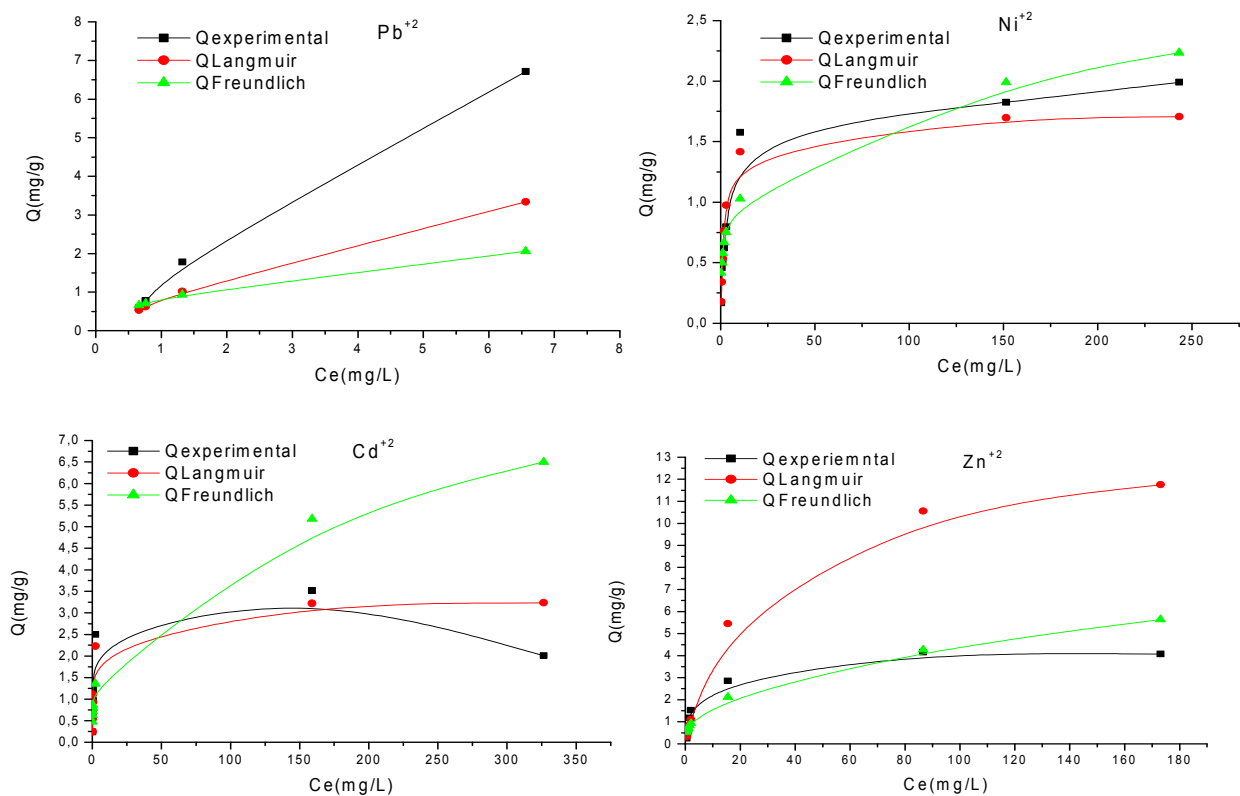

Fig. 8. Comparison of the Langmuir and Freundlich models with the experimental isotherm for Pb^{+2}, Ni^{+2}, Cd^{+2} and Zn^{+2} in a multimetal solution on green coconut shell powder treated with NaOH 0.1 mol.L^{-1}/3 h, pH 5, $C_{biomass}$ = 40 g.L^{-1}, particle size 60-99 mesh, ambient temperature (28±2 °C).

The experimental data for single systems clearly show that the Langmuir-type isotherms describe well the adsorption mechanism Pb^{+2}, Cd^{+2} and Cu^{+2}, while Zn^{+2} is of the Freundlich-type. On the other hand, Ni^{+2} agrees well with both models. The adsorption capacity of the single metals studied followed the order: $Cd^{+2} > Zn^{+2} > Cu^{+2} > Pb^{+2} > Ni^{+2}$, which can be correlated to the ionic radius of Pauling, except for Pb^{+2} and Ni^{+2} (Table 2) (Vázques et al., 2002; Mohan & Singh, 2002; Sekhar et al., 2003; Mattuschka & Straube, 1993).

The values of R_L for single and multi-metal ions are all between 0 and 1 indicating that adsorption on green coconut shell powder is very efficient for these systems (Table 4).

Metal ions	Langmuir					Freundlich			
	K_L (L mg^{-1})	q_{max} (mg g^{-1})	R_L	P	R^2	K_F (mg$^{1-(1/n)}$ (g^{-1})L$^{1/n}$)	$1/n$	P	R^2
Single metal									
Cu^{+2}	0.006	7.34	0.400-0.952	8.52	0.98	0.072	0.82	12.73	0.96
Ni^{+2}	0.015	1.23	0.214-0.891	9.22	0.97	0.028	0.76	10.89	0.93
Pb^{+2}	0.005	19.92	0.291-0.925	10.26	0.98	0.253	0.61	17.14	0.93
Cd^{+2}	0.002	1.07	0.180-0.868	9.20	0.95	0.044	0.58	16.62	0.90
Muti-metal									
Cu^{+2}	0.06	1.10	0.062-0.689	18.97	0.89	0.080	0.64	21.54	0.77
Ni^{+2}	0.03	0.59	0.082-0.939	26.14	0.54	0.009	0.97	20.46	0.89
Pb^{+2}	0.062	12.66	0.614-0.979	23.58	0.74	0.009	1.00	18.77	0.65
Cd^{+2}	0.002	1.17	0.158-0849	29.20	0.66	0.044	0.58	16.62	0.91

R_L =separation factor

Table 6. Adsorption isotherms parameters of Langmuir and Freundlich, for single-metal adsorbed on sugar cane bagasse.

Adsorption	Langmuir				Freundlich		
	K_F (mg$^{1-(1/n)}$ (g^{-1}) L$^{1/n}$)	q_{max}(mg.g^{-1})	R_L	R^2	K_F (mg$^{1-(1/n)}$ (g^{-1}) L$^{1/n}$)	$1/n$	R^2
ingle metal							
Cu^{+2}	0.072	10.45	0.441 – 0.013	0.994	0.767	0.614	0.958
Ni^{+2}	0.110	6.71	0.339 – 0.010	0.986	0.685	0.547	0.986
Pb^{+2}	0.086	8.32	0.560 – 0.01	0.986	0.814	1.492	0.925
Cd^{+2}	0.085	17.51	0.865 – 0.154	0.979	1.315	0.669	0.880
Zn^{+2}	0.072	10.45	0.697 – 0.060	0.994	0.767	0.614	0.958
Multi- metal							
Cu^{+2}	0.227	5.09	0.354 – 0.004	0.969	0.834	0.581	0.977
Ni^{+2}	0.451	1.72	0.241 – 0.003	0.967	0.580	0.245	0.900
Pb^{+2}	0.112	7.89	0.560 – 0.008	0.972	0.812	0.497	0.886
Cd^{+2}	0.962	3.24	0.098 – 0.001	0.991	1.04	0.315	0.759
Zn^{+2}	0.045	13.3	0.677 – 0.025	0.896	0.877	0.341	0.903

Table 7. Adsorption isotherms parameters of Langmuir and Freundlich, with the correlation coefficients (R^2) for single and multi-metal adsorbed on coconut shells bagasse.

3.2.4 Prediction of multi metal equilibrium

In the practice, the adsorption metal ions from wastewater generally involve the simultaneous presence of metal ions in wastewater promoting a competition between different metal ions by adsorption site. However, study of equilibrium modeling of multi-metal ions is essential for understand the real system, but usually are neglected (Frebianto,

2009). The competitive adsorption of metal ions on the sugar cane bagasse was studied (Sousa et al., 2011) using the extended Langmuir model, expressed as:

$$q_i = \frac{q_m K_i C_i}{1 + \sum_{j=1}^{n} K_j C_j} \tag{23}$$

for i = 1,2,…, n, where i and j represent the metal ions, q_i and q_m they are the adsorption capacity and maximum capacity of adsorption (mg metal / g adsorbent) and K Langmuir constant.

Considering that a solid adsorbent has a given surface area, then the presence of other solutes implies a competition for available adsorption sites. In general, the presence of other solutes decreases the adsorption of any given solute (Cooney, 1993). Based on the isotherms showed in Fig. 9 (a,b) can be seen that there is a substantial difference between predicted and experimental values indicating a considerable effect of competition by metals adsorption sites. The results showed in Figure 8 prove competition for binding sites from comparison of the experimental and predicted data. Thus, adsorption is not specific and limited to a maximum binding capacity.
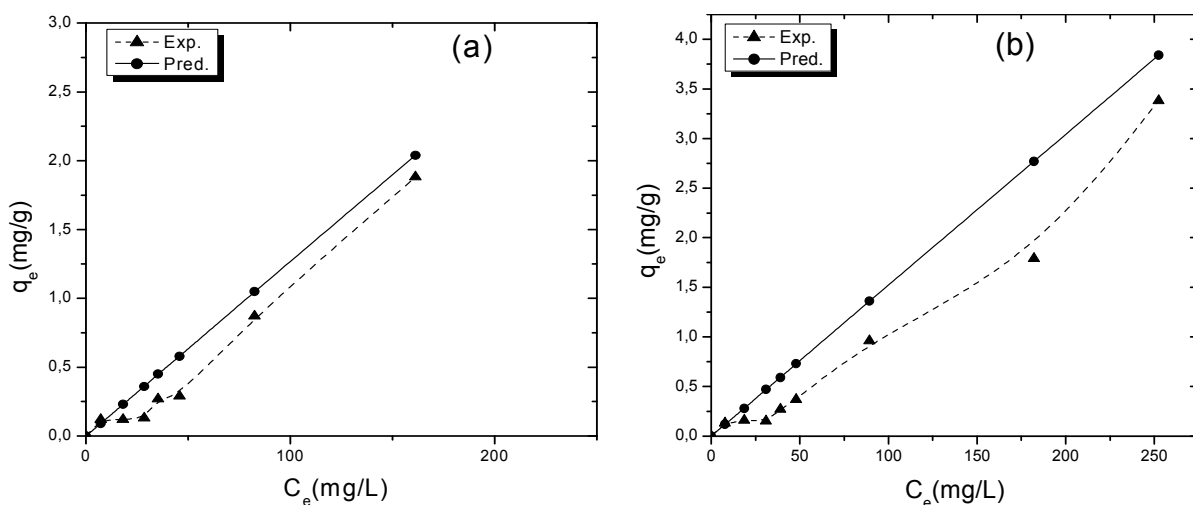

Fig. 9. Comparison between the experimental and predicted adsorption models for Ni^{+2} (a) and Cd^{+2} (b) on cane sugar bagasse treated with NaOH 0.1 mol.L⁻/3h, in a multimetal solution. Conditions: pH 5, $C_{biomass}$ = 40g.L⁻¹, ambient temperature (28±2 °C).

3.3 Adsorption in fixed bed – column

3.3.1 Breakthrough curves theory

The majority of adsorption studies have been carried out in the batch mode, but a fixed bed conventional system (column) should be economically most valuable for wastewater treatment (Cooney, 1999). A system of fixed bed conventional is compound of a column which particles of the bioadsorbent are putting in contact with the effluent. The column efficiency is described through of the concept of breakthrough curve. An ideal breakthrough curve is show in the Fig. 10, where C_o and V_e are the adsorbate concentration in the effluent and the volume of effluent passed in the column, respectively. The ideal curve admits that the adsorbate removal is complete above of the initial stages of operation. In this curve the breakpoint has been chosen arbitrarily at C_b and occur when the effluent concentration

reached 5% of the initial concentration C_o. The column reaches the complete saturation when the concentration C_x, closely approaching C_o. The total amount of effluent, V_b, passed in the column until the breakpoint and the nature of the breakthrough curve between the values of V_b and V_x are important to design of a column (Cooney, 1999).
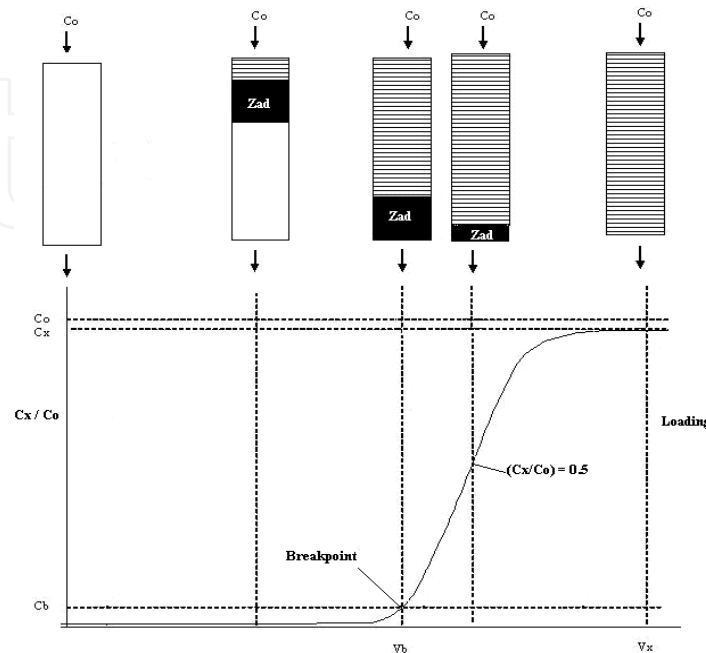

Fig. 10. Ideal breakthrough curve. (Adaptaded from Cooney, D.O.(1999). *Adsorption design for wastewater treatment* , Lewis publishers, ISBN 1566703336 9781566703338. Boca Raton, Fl and McKay, G. (1996) (Editors), Design of adsorption contatacting systems,in: Use of Adsorbents for the Rremoval of Pollutans from Wasterwaters,pp 99-131,CRC press,Inc, Boca Raton, Florida ISBN: 0-8493-6920-7

The part between C_x (exhaustion point) and C_b (breakpoint) is called the primary adsorption zone (PAZ) and the time needed for PAZ to move down the column is calculated by Equation 24 (Gupta *et al.*, 1997; 2000; Kundu & Gupta, 2005):

$$t_x = \frac{V_x}{F_m}$$

(24)

Where, t_x is the time to establish PAZ (min), F_m is the flow rate (mL/min) and V_x is the exhaustion volume (mL).

The maximum capacity of removal of toxic metal ions in the column is given by Equation 25 (Gupta *et al.*, 1997; 2000; Kundu & Gupta, 2005):

$$Q = \frac{C_0 * V}{m_s} \int_{t=0}^{t=x} (1 - \frac{C}{C_0})dt$$

(25)

Where, Q is the maximum adsorption capacity (mg/g); C_0 and C are the initial concentration of the solution and the concentration of the metal ion in a determined volume (mg/L), respectively; m_s is the mass of the adsorbent (g); V is the flow rate (L/min) and t is the time in minutes.

3.3.2 Breakthrough curves

Metal cyanides can occur of various forms in the wastewaters, generated from electroplating industries, depending of the solution pH (Patil & Paknikar, 1999; Bose et al., 2002). For wastewaters containing high copper concentration and relative concentration of zinc, nickel and cyanide, the weak complexes of nickel and zinc are present in negligible concentrations. In contrast, copper-cyanide complexes are present in appreciable quantity, due to high affinity of copper by cyanide (Bose et al., 2002).

Since the electroplating wastewater contains metal-cyanide complexes, thus the influence of these species on metal ions removal of wastewater using sugar cane bagasse have been studied (Sousa et al., 2010). For this, the breakthrough curves were investigated for synthetic effluent spiked with amount known of copper, nickel and cyanide ions similarly to the effluent industrial composition. The synthetic samples were treated by alkaline chlorination for destruction of cyanide (Akcil, 2003). The treatment of the synthetic sample was carried out with NaOCl 2M by overnight for total oxidation of cyanide (18 mg/L^{-1}) to inorganic carbon. The precipitated metal was dissolved with 1.0 mol.L^{-1} H$_2$SO$_4$ to yield a final solution with metal concentrations of 200mg.L^{-1}, 14.4 mg.L^{-1} and 65.5 mg.L^{-1} of Cu^{2+}, Ni^{2+} and Zn^{2+}, respectively. Volumes of 200mL were percolated through a column (with 4.0g of adsorbent) at flow rate of 2.0 mL min^{-1} and 10 mL eluted volume was collected at the exit of the bed column to obtain the breakthrough curves given in Fig. 11 (a,b). It is seen that the column capacity at complete exhaustion reached a plateau when the sample volume was about 70.0 mL of the effluent. The percentages of saturation of the column, calculated at breakpoint were 73.7, 75.2, and 67.5% for copper, nickel and zinc respectively.

The adsorption capacities for the metal ions obtained from breakthrough curves are shown in Table 8. It is observed that copper adsorption by cane sugar bagasse is higher than zinc and nickel adsorption (in absence and presence of cyanide). The copper ion interacts strongest with cyanide to form copper-cyanide complexes (anionic) in aqueous solutions on dependency of pH. Therefore, a considerable removal of copper in solution containing cyanide, in acidic conditions, may be due to the formation from insoluble specie CuCN (Bose et al., 2002). However, the contrast can be observed for zinc and nickel, which form relatively weak complexes with cyanide in aqueous solutions at low pH. Zinc and nickel cyanides complexes are much weaker than copper cyanide complexes, and these metals predominantly exist in the free form (uncomplexed) in presence of cyanide. Thus, a considerable decline in the adsorption of zinc and nickel on the bagasse surface (at pH 1.26) could be due to the electrostatic repulsion between the sugarcane bagasse surface (positively charged) and the free zinc and nickel ions (cations).

Synthetic wastewater	Cu(II) (200 mg/L^{-1})	Ni(II) (14.5 mg/L^{-1})	Zn(II) (45.5mg/L^{-1})	CN$^-$ (18.1mg/L^{-1})
	q (mg metal / g adsorbent)			
Initial	1.85	0.145	0.421	_
with cyanide	1.89	0.134	0.412	18.1
After cyanide removal	2.04	0.144	0.443	ND

Table 8. Adsorption capacities of toxic metal ions from simulated electroplating wastewater using sugar cane bagasse. Conditions: pH 1.26; flow: 2.0 mL/min; mass of the adsorbent: 4.0g; temperature: 28 ±2ºC.
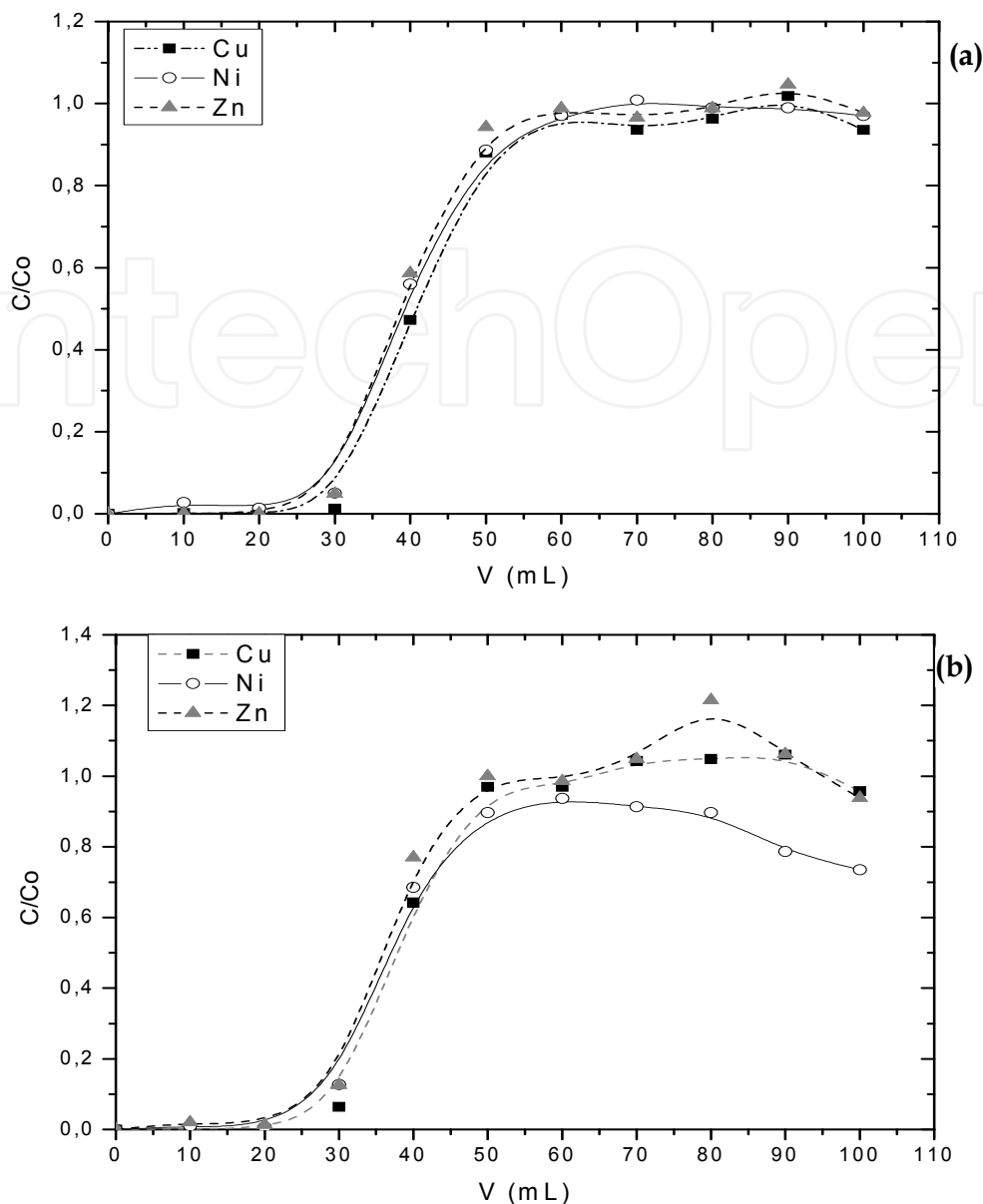
Fig. 11. Breakthrough curves of metals. (a) wastewater with cyanide (18 mg/L) and (b) wastewater after NaOCl oxidation of cyanide. Amount of adsorbent 4.0g, Cu⁺² concentration 200 mg/L at pH 1.78 and flow rate of 2.0mL/min. C/C_o represent the ion concentrations for initial and final solution. (Adaptaded from Sousa et al., 2009. Journal Environment Manager, Vol. 90, N° 11, pp. 3340–3344, ISSN 0301-4797)

3.3.3 Column application in samples industrial

Electroplating wastewater contains metal ions, then an effective removal of these species is necessary. For testing the treatability from an wastewater industrial (Juazeiro do Norte – Ceara -Brazil) containing Cu- Ni-Zn with sugar cane bagasse, thus 250 mL wastewater were passed on column in conditions as described previously to obtain the breakthrough. 60 mL of the final solution for both metals, at pH 1.5, were sufficient to saturate the amount of adsorbent (4.0 g) on column. Table 9 shows the metals ions removal (Cu, Ni and Zn) from an electroplating-wastewater industrial (Juazeiro do Norte – Ceara -Brazil) by sugar cane

bagasse. For testing the treatability from an wastewater industrial was employed a polyethylene column (10cm x 0.8 cm D.I) packed with 0.30g of adsorbent (bed depth of 6 cm) at flow rate 1.0 mL/min^{-1} at pH 5. It is observed in Table 9 that the copper removal varied 42.4 to 90.8% and 13.7 to 52.6% for nickel from wastewaters.

Metal ion	Conc.	Wastewater samples							
		1	2	3	4	5	6	7	8
	C_o (mg L^{-1})	73.03	17.44	147.03	3.95	17.84	0.46	0.43	40.99
Cu	C_e (mg L^{-1})	19.77	1.60	36.75	0.41	2.02	-	0.099	5.39
	Removal,%	72.92	90.80	75.00	89.70	88.69	-	77.35	86.84
	C_o (mg L^{-1})	38.45	1.15	17.94	1.52	1.62	2.28	1.58	0.82
Ni	C_e (mg L^{-1})	18.98	0.77	9.09	0.77	0.91	1.34	0.75	-
	Removal,%	50.64	33.21	49.33	49.62	43.96	41.14	52.59	-
	C_o (mg L^{-1})	40.13	10.53	31.29	-	-	-	-	-
Zn	C_e (mg L^{-1})	7.15	3.34	7.26	-	-	-	-	-
	Removal,%	82.19	68.11	76.80	-	-	-	-	-

Table 9. Metals removal from industrial wastewaters collected from galvanic industries (Juazeiro do Norte- Ceara-Brazil). Conditions: Polyethylene column (10cm x 0.8 cm D.I, packed with 0.30g adsorbent) in the conditions described in previously

3.3.4 Column regeneration and metal recovery

Metal recoveries and the column regeneration were carried out by acid elution method (HCl 0.1M, HNO$_3$ 0.1M), under conditions tested for breakthrough curve, with synthetic solution. The results obtained are shown in Fig.12, 30 mL of acid eluent is efficient for almost complete desorption of the retained metals. Also is noted that the first aliquot of 5 mL elutes more 70 % of retained ions on column, while the remaining eluant volume (25 mL) desorbed the rest
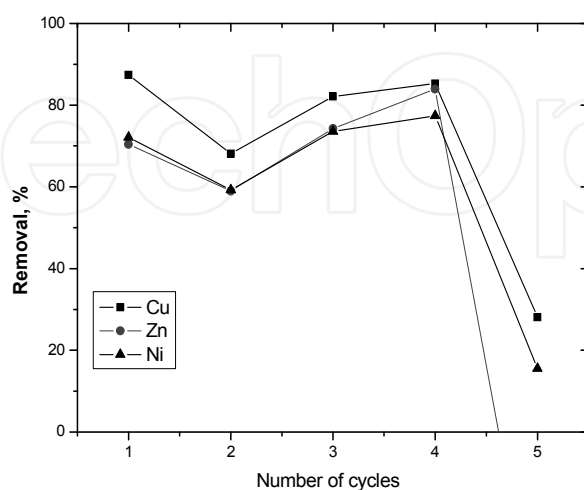

Fig. 12. Removal efficiency with number of cycles for metal ions on cane sugar bagasse from wastewater ((Adaptaded from Sousa et al., 2009. Journal Environment Manager, Vol. 90, N° 11, pp. 3340–3344, ISSN 0301-4797)

of ions. A test for check the recycling of the adsorbent on column was carried out to passing first water (30 mL) on column, and 60 mL of sample solution without treatment, and HCl 2M (70mL) to the elution of metals retained, this procedure was repeated 5 times with the same adsorbent of the column. The results shown in Fig.11, indicate that the removal efficiency decreases from 79.6% to 65 for (Cu), 77.4 to 66.7 % for (Zn) and 73,8 % for (Ni) during their first to fourth cycles. In contrast, a lost drastically of efficiency of the adsorbent was observed after 4 cycles.

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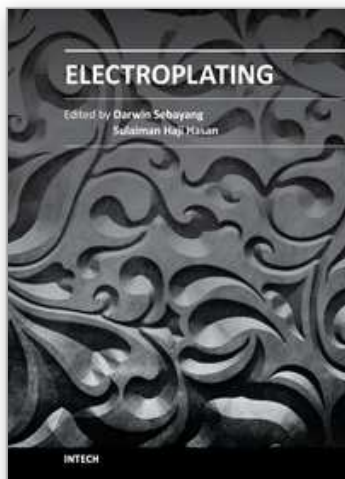
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