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Review

Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions – A review

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Abstract

Heavy metal remediation of aqueous streams is of special concern due to recalcitrant and persistency of heavy metals in environment. Conventional treatment technologies for the removal of these toxic heavy metals are not economical and further generate huge quantity of toxic chemical sludge. Biosorption is emerging as a potential alternative to the existing conventional technologies for the removal and/or recovery of metal ions from aqueous solutions. The major advantages of biosorption over conventional treatment methods include: low cost, high efficiency, minimization of chemical or biological sludge, regeneration of biosorbents and possibility of metal recovery. Cellulosic agricultural waste materials are an abundant source for significant metal biosorption. The functional groups present in agricultural waste biomass viz. acetamido, alcoholic, carbonyl, phenolic, amido, amino, sulphydryl groups etc. have affinity for heavy metal ions to form metal complexes or chelates. The mechanism of biosorption process includes chemisorption, complexation, adsorption on surface, diffusion through pores and ion exchange etc. The purpose of this review article is to provide the scattered available information on various aspects of utilization of the agricultural waste materials for heavy metal removal. Agricultural waste material being highly efficient, low cost and renewable source of biomass can be exploited for heavy metal remediation. Further these biosorbents can be modified for better efficiency and multiple reuses to enhance their applicability at industrial scale.

Keywords: Agricultural wastes; Biosorption; Industrial effluents; Heavy metal remediation; Adsorbent

1. Introduction

Toxic heavy metal ions get introduced to the aquatic streams by means of various industrial activities viz. mining, refining ores, fertilizer industries, tanneries, batteries, paper industries, pesticides etc. and posses a serious threat to environment (Celik and Demirbas, 2005; Friedman and Waiss, 1972; Kjellstrom et al., 1977; Pastircakova, 2004). The major toxic metal ions hazardous to humans as well as other forms of life are Cr, Fe, Se, V, Cu, Co, Ni, Cd, Hg, As, Pb, Zn etc. These heavy metals are of specific concern due to their toxicity, bio-accumulation tendency and persistency in nature (Friberg and Elinder, 1985; Garg et al., 2007; Randall et al., 1974). Several past disasters due to the contamination of heavy metals in aquatic streams are Minamata tragedy in Japan due to methyl mercury contamination and "Itai-Itai" due to contamination of cadmium in Jintsu river of japan (Friberg and Elinder, 1985; Kjellstrom et al., 1977). Various regulatory bodies have set the maximum prescribed limits for the discharge of toxic heavy metals in the aquatic systems. However the metal ions are being added to the water stream at a much higher concentration than the prescribed limits by industrial activities, thus leading to the health hazards and environmental degradation (Table 1).

Conventional methods for removal of metal ions from aqueous solutions include chemical precipitation, ion exchangers, chemical oxidation/reduction, reverse osmosis, electro dialysis, ultra filtration etc (Gardea-Torresdey et al., 1998; Patterson, 1985; Zhang et al., 1998). However these

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Table 1
Permissible limits and health effects of various toxic heavy metals

Metal contaminant	Permissible limits for industrial effluent discharge (in mg/l)			Permissible limits by international bodies (μg/l)		Health hazards
	Into inland surface waters Indian Standards: 2490(1974)	Into public sewers Indian Standards: 3306(1974)	On land for irrigation Indian Standards: 3307 (1974)	WHO	USEPA	
Arsenic	0.20	0.20	0.20	10	50	Carcinogenic, producing liver tumors, skin and gastrointestinal effects
Mercury	0.01	0.01	–	01	02	Corrosive to skin, eyes and muscle membrane, dermatitis, anorexia, kidney damage and severe muscle pain
Cadmium	2.00	1.00	–	03	05	Carcinogenic, cause lung fibrosis, dyspnea and weight loss
Lead	0.10	1.00	–	10	05	Suspected carcinogen, loss of appetite, anemia, muscle and joint pains, diminishing IQ, cause sterility, kidney problem and high blood pressure
Chromium	0.10	2.00	–	50	100	Suspected human carcinogen, producing lung tumors, allergic dermatitis
Nickel	3.0	3.0	–	–	–	Causes chronic bronchitis, reduced lung function, cancer of lungs and nasal sinus
Zinc	5.00	15.00	–	–	–	Causes short-term illness called "metal fume fever" and restlessness
Copper	3.00	3.00	–	–	1300	Long term exposure causes irritation of nose, mouth, eyes, headache, stomachache, dizziness, diarrhea

conventional techniques have their own inherent limitations such as less efficiency, sensitive operating conditions, production of secondary sludge and further the disposal is a costly affair (Ahluwalia and Goyal, 2005a). Another powerful technology is adsorption of heavy metals by activated carbon for treating domestic and industrial waste water. (Horikoshi et al., 1981; Hosea et al., 1986). However the high cost of activated carbon and its loss during the regeneration restricts its application. Since 1990's the adsorption of heavy metal ions by low cost renewable organic materials has gained momentum (Bailey et al., 1999; Orhan and Bujukgungor, 1993; Rao and Parwate, 2002; Vieira and Volesky, 2000). The utilization of seaweeds, moulds, yeasts, and other dead microbial biomass and agricultural waste materials for removal of heavy metals has been explored (Bailey et al., 1999; Haung and Haung, 1996; Sudha and Abraham, 2003; Zhou and Kiff, 1991). Recently attention has been diverted towards the biomaterials which are byproducts or the wastes from large scale industrial operations and agricultural waste materials. The major advantages of biosorption over conventional treatment methods include: low cost, high efficiency, minimization of chemical or biological sludge, no additional nutrient requirement, and regeneration of biosorbents and possibility of metal recovery.

Agricultural materials particularly those containing cellulose shows potential metal biosorption capacity. The basic components of the agricultural waste materials biomass include hemicellulose, lignin, extractives, lipids, proteins, simple sugars, water hydrocarbons, starch containing variety of functional groups that facilitates metal complexation which helps for the sequestering of heavy metals (Bailey et al., 1999; Hashem et al., 2005a,b, 2007). Agricultural waste materials being economic and eco-friendly due to their unique chemical composition, availability in abundance, renewable, low in cost and more efficient are seem to be viable option for heavy metal remediation. Studies reveal that various agricultural waste materials such as rice bran, rice husk, wheat bran, wheat husk, saw dust of various plants, bark of the trees, groundnut shells, coconut shells, black gram husk, hazelnut shells, walnut shells, cotton seed hulls, waste tea leaves, *Cassia fistula* leaves, maize corn cob, jatropa deoiled cakes, sugarcane bagasse, apple, banana, orange peels, soybean hulls, grapes stalks, water hyacinth, sugar beet pulp, sunflower stalks, coffee beans, arjun nuts, cotton stalks etc has been tried (Annadurai et al., 2002; Cimino et al., 2000; Hashem et al., 2006a,b; Macchi et al., 1986; Maranon and Sastre, 1991; Mohanty et al., 2005; Orhan and Bujukgungor, 1993; Reddad et al., 2002; Tee and Khan, 1988). These promising agricultural waste materials are used in the removal of metal ions either in their natural form or after some physical or chemical modification. The present review article deals with the utilization of agricultural waste materials as biosorbents for removal of toxic heavy metal ions from aqueous streams.

2. Mechanism of biosorption

The removal of metal ions from aqueous streams using agricultural materials is based upon metal biosorption (Volesky and Holan, 1995). The process of biosorption involves a solid phase (sorbent) and a liquid phase (solvent) containing a dissolved species to be sorbed. Due to high affinity of the sorbent for the metal ion species, the latter is attracted and bound by rather complex process affected by several mechanisms involving chemisorption, complexation, adsorption on surface and pores, ion exchange, chelation, adsorption by physical forces, entrapment in inter and intrafibrillar capillaries and spaces of the structural polysaccharides network as a result of the concentration gradient and diffusion through cell wall and membrane (Basso et al., 2002; Sarkanen and Ludwig, 1971; Qaiser et al., 2007) (Fig. 1).

Agricultural waste materials are usually composed of lignin and cellulose as the main constituents. Other components are hemicellulose, extractives, lipids, proteins, simple sugars, starches, water, hydrocarbons, ash and many more compounds that contain a variety of functional groups present in the binding process. Cellulose is a crystalline homo-polymer of glucose with $\beta 1 \rightarrow 4$ glycosidic linkage and intra-molecular and intermolecular hydrogen bonds (Demirbas, 2000a,b). Hemicellulose is a heteropolymer of mainly xylose with $\beta 1 \rightarrow 4$ glycosidic linkage with other substances of acetyl feruoyl and glycouronyl groups (Garg et al., in press). Lignin is three dimensional polymer of aromatic compounds covalently linked with xylans in hardwoods and galactoglucomannans in softwoods (Garg et al., 2007; Sjötröm, 1981) The functional groups present in biomass molecules acetamido groups, carbonyl, phenolic, structural polysaccharides, amido, amino, sulphydryl carboxyl groups alcohols and esters (Beveridge and Murray, 1980; Gupta and Ali, 2000). These groups have the affinity for metal complexation. Some biosorbents are non-selective and bind to a wide range of heavy metals with no specific priority, whereas others are specific for certain types of metals depending upon their chemical composition. The presence of various functional groups and their complexation with heavy metals during biosorption process has been reported by different research workers using

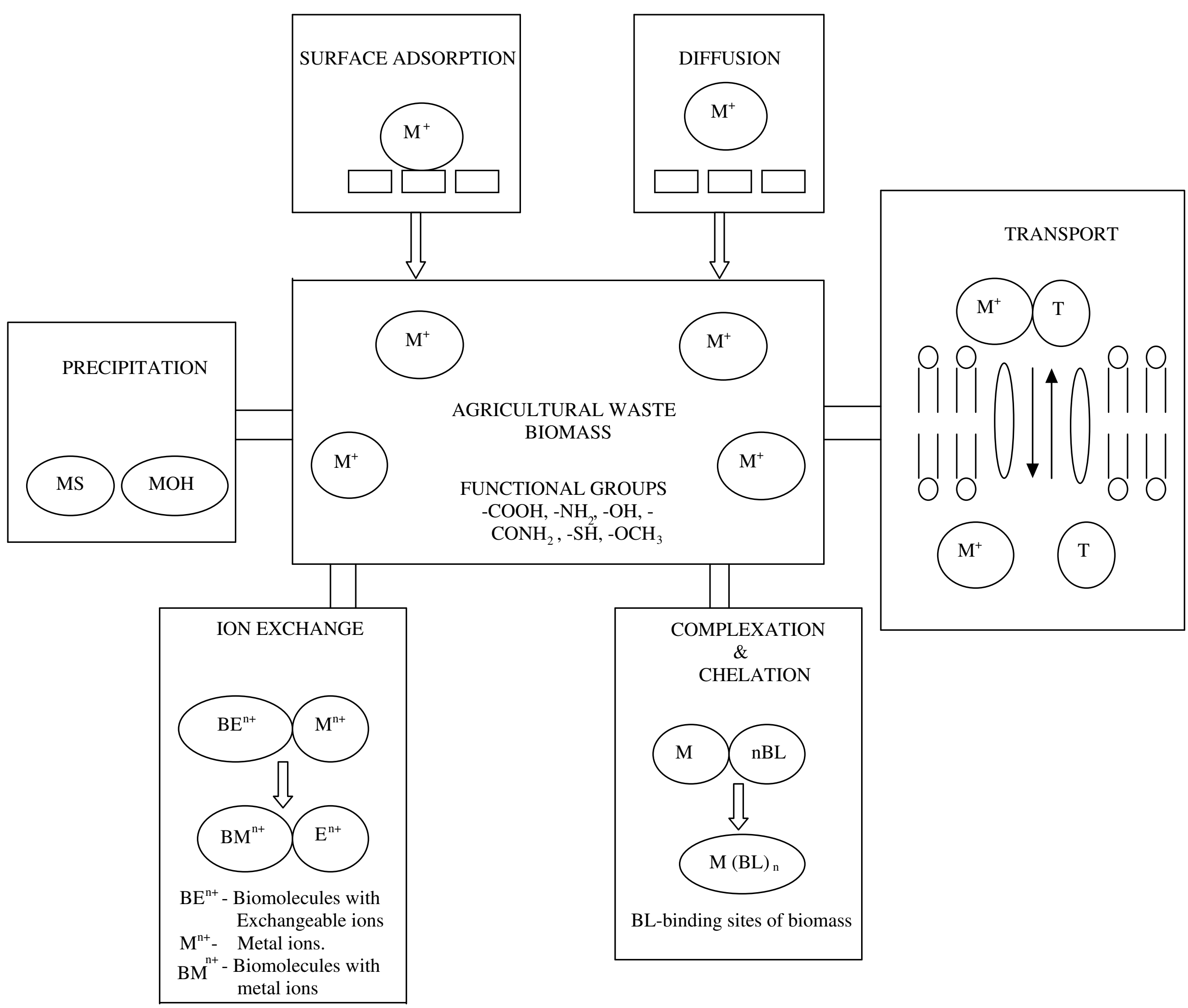

Fig. 1. Plausible mechanism of biosorption.

spectroscopic techniques (Ahluwalia and Goyal, 2005a; Garg et al., 2007; Tarley and Arruda, 2004).

3. Absorption models

Predicting the rate at which adsorption takes place for a given system is probably the most important factor in adsorption system design, with adsorbate residence time and the reactor dimensions controlled by the system's kinetics. Numerous kinetic models have described the reaction order of adsorption systems based on solution concentration. These include first-order and second-order reversible ones, and first-order and second-order irreversible ones, pseudo-first-order and pseudo-second-order. The sorption isotherms represent the relationship between the amount adsorbed by a unit weight of solid sorbent and the amount of solute remaining in the solution at equilibrium (Park et al., 2006). Both Langmuir and Freundlich isotherm models have been shown to be suitable for describing short-term and mono component adsorption of metal ions by different biosorbents (Aksu et al., 1999; Ho et al., 2002). On the other hand, reaction orders based on the capacity of the adsorbent have also been studied, such as Lagergren's first-order equation, Redlich Peterson model and BET model (Ho and Mckay, 1998). Langmuir and Freundlich isotherm models are frequently used isotherm models for describing short-term and mono component adsorption of metal ions by different materials (Aksu et al., 1999; Yu et al., 2001).

4. Thermodynamic parameters

The free energy change of sorption can be calculated by Eq. (1).

$$\Delta G^0 = -RT \ln K \tag{1}$$

where ΔG^0 is standard free energy change, R is the universal gas constant (8.314 J/mol/K), T is the absolute temperature and K is equilibrium constant. The apparent equilibrium constant of the biosorption, K'_{C} is obtained from Eq. (2).

$$K'_{\mathrm{C}} = \mathrm{C(biosorbent)eq/C(solution)} \tag{2}$$

where C (biosorbent) eq and C (solution) eq are the metal ion concentrations on the biosorbent and in the solution at equilibrium.

5. Performance of agricultural waste materials as biosorbents for the removal of heavy metals

Removal of heavy metal ions from the aqueous streams by agricultural waste materials is an innovative and promising technology. The efficiency of the waste material depends upon the capacity, affinity, and specificity including physico-chemical nature of it. Scattered research has already been done on the variety of biosorbents for the removal of metal ions as Cr, Cu, Ni, Pb, Cd, As, Hg etc. The adsorbents are taken either in the natural form, or modified by chemical and thermal treatment for increasing their sorption capabilities.

5.1. Removal of chromium

Chromium is a toxic heavy metal being released in the environment by applications like tanning, wood preservation and pigments, dyes for plastic, paints, and textiles. Chromium occurs in a number of oxidation states, but chromium (VI) and chromium (III) are of main environmental concern (Yu et al., 2000). Extensive work has been reported for the removal of chromium employing waste agricultural materials.

A number of agricultural wastes like, hazelnut shells, orange peels, maize cobs, peanut shells, soyabean hulls, jack fruit, soyabean hulls in natural or modified forms has been explored and significant removal efficiency was reported (Kurniawan et al., 2006). Diverse plant parts such as coconut fiber pith, coconut shell fiber, plant bark (*Acacia arabica*, Eucalyptus), pine needles, cactus leaves, neem leave powder have also been tried for chromium removal showing efficiency more than 90–100% at optimum pH (Dakiky et al., 2002; Manju and Anirudhan, 1997; Mohan et al., 2006a; Sarin and Pant, 2006; Venkateswarlu et al., 2007). The utilization of rice bran and wheat bran as an adsorbent are found to be less effective as only 50% removal efficiency was reported (Farajzadeh and Monji, 2004; Oliveira et al., 2005). Gardea-Torresdey et al. (2000) reported *Avena monida* (whole plant biomass) showed 90% removal efficiency of Cr VI at optimum pH 6.0. Rice husk in natural form as well as activated rice husk carbon was used for the removal of chromium (VI) and results were also compared with commercial activated carbon and other adsorbents. (Bishnoi et al., 2004; Mehrotra and Dwivedi, 1988; Srinivasan et al., 1988).

Saw dust of Indian rose wood prepared by treatment with formaldehyde and sulphuric acid showed efficient removal of chromium (VI) (Garg et al., 2004). Beech saw dust and rubber wood saw dust was also tried for chromium removal (Acar and Malkoc, 2004; Karthikeyan et al., 2005). Sugarcane bagasse was used in natural as well as modified form and efficiency for both the forms was compared for the removal of Cr. (Gupta and Ali, 2004; Krishanani et al., 2004; Rao and Parwate, 2002). Utilization of mustard oil cake has been reported with significant removal efficiency and the results of activated carbon of sugar industry waste and commercial granular activated carbon for sequestering of heavy metal ions from aqueous solutions were compared (Ajmal et al., 2005; Fahim et al., 2006). Recently sugar cane baggase, maize corn cob and jatropha oil cake as such were used for removal of chromium under optimized conditions (Garg et al., 2007).

Most of the studies showed that the chromium biosorption by agricultural waste materials is quite high and varies from 50 to 100%. Mostly biosorption occurs in acidic range particularly at pH 2.0. Thus chromium speciation plays the dominant role in deciding the removal efficiency as at pH 2 chromium is present as chromium (III). Table 2 summarizes the work reported in literature for the removal of chromium by using agricultural waste materials.

5.2. Removal of lead

The major source of lead in the environment is from plastics, finishing tools, cathode ray tubes, ceramics, solders, pieces of lead flashing and other minor product, steel and cable reclamation. Lead can result in the wide range of biological effects depending upon the level and duration of exposure (Friberg and Elinder, 1985). In the environment lead binds strongly to particles such as oil, sediments and sewage sludge so its removal is of great concern.

Different agricultural wastes viz. rice straw, soybean hulls, sugarcane bagasse, peanut shells and walnut shells in their natural form have been used for removal of lead has been reported 98% (Johns et al., 1998). Bankar and Dara (1985) conducted studies on Febrifuga tree bark in its natural form. Petioler felt sheath palm (PFP), agro waste of black gram husk, flowers of *Humulus lupulus*, waste tea leaves and water hyacinth were studied for removal of lead and efficiency of these materials varies from 70 to 98% (Ahluwalia and Goyal, 2005a; Gardea-Torresdey et al., 2002; Iqbal et al., 2002, 2005; Kamble and Patil, 2001; Saeed et al., 2005b).

Lee et al. (1999) investigated removal of lead and other metal ions by apple residues modified with phosphorous (V) oxychloride in both batch and column studies and compared the results. Rose petals pretreated with NaOH, calcium treated sargassum and sugarcane modified with succinic anhydride has also been utilized for significant removal of lead. (Karnitz et al., 2007; Nasir et al., 2007; Tsui et al., 2006). Activated carbon prepared from agricultural waste was also explored by different workers and high efficiency for removal of lead has been reported. (Gajghate et al., 1991; Kadirvelu et al., 2001; Vaughan et al., 2001; Wilson et al., 2006). Gupta et al. (1999) used bagasse fly ash for removal of lead with 65% removal efficiency. Saw dust of maple (Zhang et al., 1998), *Pinus sylvestries* (Taty-Costodes et al., 2003) and rubber wood saw dust (Raji et al., 1997) has shown 85–90% removal efficiency but results show that modification did not enhance the removal efficiency for lead. Literature studies revealed that optimized value for biosorption of lead is found around pH 5–6 (Table 3).

5.3. Removal of cadmium

Cadmium and Cadmium compounds as compared to other heavy metals are relatively water soluble therefore mobile in soil and tends to bioaccumulate. The long life time PVC-window frames, plastics and plating on steel are the basic sources of cadmium in the environment. Cadmium accumulates in the human body especially in kidneys, thus leading to disfunction of the kidney (Volesky and Holan, 1995).

Potential use of rice bran and wheat bran was tried for sequestering cadmium and significant removal efficiency was reported (Montanher et al., 2005; Farajzadeh and Monji, 2004; Singh et al., 2005). Studies were also conducted on use of rice polish, rice husk and black gram husk in their natural as well as modified form for the removal of cadmium and their relative efficiency was reported (Iqbal et al., 2005; Kumar and Bandyopadhyay, 2006; Singh et al., 2005; Tarley and Arruda, 2004). Bark of the plants such as *Pecia glehnii* and *Abies sachalinensis* and dried plant biomass of parthenium was tried for the removal of cadmium (Ajmal et al., 2006; Seki et al., 1997). Use of other parts of the plants such as peels of peas, fig leaves, broad beans, orange peels, medlar peels and jack fruits as adsorbents have been reported to show high removal efficiency at acidic pH (Benaissa, 2006).

Table 2
Summary of work done by various researchers using low cost agricultural waste materials for the removal of chromium

Agricultural waste	Metal ion	Results	Reference
Oat biomass	Cr (III), Cr (VI)	>80%	Gardea-Torresdey et al. (2000)
Formaldehyde treated saw dust Indian rosewood	Cr (VI)	62–86%	Garg et al. (2004)
Beech saw dust	Cr (VI)	100%	Acar and Malkoc (2004)
Chemically treated bagasse	Cr (VI)	50–60%	Krishanani et al. (2004)
Formaldehyde treated rice husk	Cr (VI)	88.88%	Bishnoi et al. (2004)
Bagasse fly ash	Cr (VI)	96–98%	Gupta and Ali (2004)
Wheat bran	Cr (VI)	>82%	Farajzadeh and Monji (2004)
Coconut shell fibers	Cr (VI)	>80%	Mohan et al. (2006a)
Commercial granular activated carbon (C2 & C3) and AC of waste from sugar industry (C1)	Cr (VI)	93–98% C1 > C2 > C3	Fahim et al. (2006)
Eucalyptus bark	Cr (VI)	Almost 100%	Sarin and Pant (2006)
Neem leaf powder	Cr (VI)	>96%	Venkateswarlu et al. (2007)
Rubber wood saw dust	Cr (VI)	60–70%	Karthikeyan et al. (2005)
Pretreated bagasse with NaOH and CH_3COOH	Cr (VI), Ni (II)	90%, 67%	Rao et al. (2002)
Modified bagasse fly ash	Cr (VI)	67%	Gupta et al. (1999)
Activated carbon from bagasse (carbonization & gasification)	Cr (VI)	Significant metal uptake	Valix et al. (2006)
Sugarcane bagasse, maize corn cob, jatropha oil cake	Cr (III)	Upto 97%	Garg et al. (2007)
Raw rice bran	Cr (VI), Ni (II)	40–50%	Oliveira et al. (2005)

Table 3
Summary of work done by various researchers using variety of agricultural waste materials for the removal of Lead

Agricultural waste	Metal ion	Results	Reference
Oriza sativa husk	Pb (II)	98%	Zulkali et al. (2006)
Agricultural by product *Humulus lupulus*	Pb (II)	75%	Gardea-Torresdey et al. (2002)
Chemical modified apple residue waste	Pb (II)	Upto 80%	Lee et al. (1999)
Agro waste of black gram husk	Pb (II)	Upto93%	Saeed et al. (2005b)
Febrifuga bark	Pb (II)	100%	Bankar and Dara (1985)
Chemically modified saw dust of rubber wood	Pb (II)	85%	Raji and Anirudhan (1998)
Coconut char based activated carbon	Pb (II)	100%	Gajghate et al. (1991)
Rose biomass pretreated with NaOH	Pb, Zn (II)	75%	Nasir et al. (2007)
Rice bran	Pb (II), Cd (II), Cu (II), Zn (II)	>80.0%	Montanher et al. (2005)
Saw dust of *Pinus sylvestris*	Pb (II), Cd (II)	96%, 98%	Taty-Costodes et al. (2003)
Maple saw dust	Pb (II), Cu (II)	80–90% 60–90%	Yu et al. (2001)
Water hyacinth	Pb (II), Cu (II), Co (II), Zn (II)	70–80%	Kamble and Patil (2001)
Low cost sorbents (bark, dead biomass, chitin, sea weed, algae, peat moss, leaf mould, moss, zeolite, modified cotton) etc.	Pb (II), Cd (II), Cr (VI), Hg (II)	Good results	Bailey et al. (1999)
Waste tea leaves	Pb (II), Fe (II), Zn (II), Ni (II)	92%, 84%, 73%	Ahluwalia and Goyal (2005b)
Activated carbon from coir pith	Pb (II), Hg (II), Cd (II), Ni (II), Cu (II)	Hg-100% Pb-100% Cu-73% Ni-92% Cd- !00%	Kadirvelu et al. (2001)
Rice straw, soybean hulls, sugarcane bagasse, peanut shells, pecan and walnut shells	Pb (II), Cu (II), Cd (II), Zn (II), Ni (II)	Pb > Cu > Cd > Zn > Ni	Johns et al. (1998)
PFP (petiolar felt sheath palm)-peelings from trunk of palm tree	Pb (II), Cd (II), Cu (II), Zn (II), Ni (II), Cr (VI)	>70% Pb > Cd > Cu > Zn > Ni > Cr	Iqbal et al. (2002)
Activated carbon of peanut shells	Pb (II), Cd (II), Cu (II), Ni (II), Zn (II)	Upto 75%	Wilson et al. (2006)

Adsorption experiments conducted on hazelnut shells, peanut hulls, walnut shells, and green coconut shells gave significant results for removal of cadmium (Johns et al., 1998; Kurniawan et al., 2006). Studies were conducted on activated carbon of bagasse pith, coir pith, peanut shells and dates and their removal efficiency varies from 50 to 98% (Kadirvelu et al., 2001; Kannan and Rengasamy, 2005; Krishnan and Anirudhan, 2003; Mohan and Singh, 2002; Srivastva et al., 1996; Wafwoy et al., 1999). Research has also been carried out by using chemically treated agricultural waste materials like base treated rice husk, treated juniper fibers, and corncob modified with citric acid, modified peanut shells, succinic anhydride treated sugarcane etc. (Karnitz et al., 2007; Min et al., 2004; Vaughan et al., 2001).

Most of the studies showed that agricultural waste either in natural form or modified form is highly efficient for the removal of cadmium metal ions. Summary of research work done has been compiled in Table 4.

5.4. Removal of nickel

Nickel and its compounds have no characteristic odor or taste. The sources of nickel to the environment are nickel plating, colored ceramics, batteries, furnaces used to make alloys or from power plants and trash incinerators. The most harmful health effect of nickel is the allergic reactions (Akhtar et al., 2004).

Experiments on removal of nickel were conducted on *Cassia fistula* biomass in its natural form and results show 99–100% removal efficiency (Hanif et al., 2007). Waste tea leaves were also tried for sequestering of nickel from aqueous solutions (Ahluwalia and Goyal, 2005a). Saw dust of maple, oak and black locust have been reported as promising biosorbent for removal of nickel (Sciban et al., 2006; Shukla et al., 2005). Agricultural wastes such as peanut, pecan, walnut, hazelnut and groundnut shells in natural or modified form were also utilized for biosorption (Demirbas et al., 2002; Johns et al., 1998; Kurniawan et al., 2006; Shukla and Pai, 2005). Other agricultural waste materials as modified coir fibers, cotton seeds, soyabeans and corncobs have also been explored for removal of nickel (Marshall and Johns, 1996; Shukla et al., 2005; Vaughan et al., 2001). Sugar cane bagasse in its natural form showed more than 80% removal efficiency (Garg et al., 2007). Table 5 is a compilation of research work done on the removal of nickel.

Table 4
Summary of work done by various researchers using variety of agricultural waste materials for the removal of cadmium

Agricultural waste	Metal ion	Results	Reference
Peels of peas, fig leaves, broad beans, medlar peel	Cd (II)	70–80%	Benaissa (2006)
Wheat bran	Cd (II)	87.15%	Singh et al. (2005)
Three kinds treated rice husk	Cd (II)	80–97%	Kumar and Bandyopadhyay (2006)
Rice polish	Cd (II)	>90%	Singh et al. (2005)
Steam activated sulphurised carbon (SA–S–C) from bagasse pith	Cd (II)	98.8%	Krishnan and Anirudhan (2003)
Base treated juniper fiber	Cd (II)	High removal capacity	Min et al. (2004)
Husk of black gram	Cd (II)	99%	Saeed and Iqbal (2003)
Straw, saw dust, datesnut	Cd (II)	>70%	
Dried parthenium powder	Cd (II)	>99%	Ajmal et al. (2006)
Bagasse fly ash	Cd (II), Ni (II)	65 & 42%	Srivastava et al. (2007)
Bagasse	Cd (II), Zn (II)	90–95%	Mohan and Singh (2002)
Bagasse fly ash	Cd (II), Ni (II)	90.0%	Gupta et al. (2003)
Rice bran	Cd (II), Cu (II), Pb (II), Zn (II)	>80.0%	Montanher et al. (2005)
Wheat bran	Cd (II), Hg (II), Pb (II), Cr (VI), Cu (II), Ni (II)	>82% except Ni	Farajzadeh and Monji (2004)
Hazelnut shell, orange peel, maize cob, peanut hulls, soyabean hulls treated with NaOH & jack fruits	Cd (II), Cr (VI), Cu (II), Ni (II), Zn (II)	High metal adsorption	Kurniawan et al. (2006)
Papaya wood	Cd (II), Cu (II), Zn (II)	98, 95, 67%	Saeed et al. (2005a)
Rice straw, soybean hulls, sugarcane bagasse, peanut shells, pecan and walnut shells	Cd (II), Pb (II), Cu (II), Zn (II), Ni (II)	Pb > Cu > Cd > Zn > Ni	Johns et al. (1998)
Poplar wood saw dust	Cd (II), Cu, Zn (II)	Cu > Zn > Cd	Sciban et al. (2007)
Chemically modified sugarcane with succinic anhydride	Cd (II), Cu (II), Pb (II)	>80%	Karnitz et al. (2007)
Powder of green coconut shell	Cd (II), Cr (II), As (II)	98%	Pino et al. (2006)
Bark of *Abies sachalinensis* & *Pecia glehnii*	Cd (II), Cu (II), Zn (II), Ag (II), Mn (II), Ni (II)	Upto 63%	Seki et al. (1997)

Table 5
Summary of work done by various researchers using variety of agricultural waste materials for the removal of nickel

Agricultural waste	Metal ion	Results	Reference
Hazelnut shell activated carbon	Ni (II)	Effective removal	Demirbas et al. (2002)
Casia fistula biomass	Ni (II)	100%	Hanif et al. (2007)
Maple saw dust	Ni (II)	75%	Shukla et al. (2005)
Sugarcane bagasse	Ni (II)	>80%	Garg et al. (2007)
Tea waste	Ni (II)	86%	Malkoc and Nuhoglu (2005)
Defatted rice bran, chemically treated soybean & cottonseed hulls	Ni (II), Zn (II), Cu (II)	57%, 87%	Marshall and Johns (1996)
Waste tea leaves	Ni (II), Pb (II), Fe (II), Zn (II)	92%, 84%, 73%	Ahluwalia and Goyal (2005a)
Saw dust of oak and black locust hard wood (modified & unmodified)	Ni (II), Cu (II), Zn (II)	70–90%	Sciban et al. (2006)
Hazelnut shell, orange peel, maize cob, peanut hulls, soyabean hulls treated with NaOH & jack fruits	Ni (II), Cr (II), Cu (II), Cd (II), Zn (II)	High metal adsorption	Kurniawan et al. (2006)
Mustard oil cake	Ni (II), Cu (II), Zn (II), Cr (II), Mn (II), Cd (II), Pb (II)	Upto 94%	Ajmal et al. (2005)
Coir fiber chemically modified with hydrogen peroxide	Ni (II), Zn (II), Fe (II)	>70%	Shukla et al. (2005)
Dye loaded groundnut shells and saw dust	Ni (II), Cu (II), Zn (II)	Up to 90%	Shukla and Pai (2005)
PFP (petiolar felt sheath palm)-peelings from trunk of palm tree	Ni (II), Pb (II), Cd (II), Cu (II), Zn (II), Cr (VI)	>70% Pb > Cd > Cu > Zn > Ni > Cr	Iqbal et al., 2002
Agro waste of black gram husk	Ni (II), Pb (II), Cd (II), Cu (II), Zn (II)	Upto93%	Saeed et al. (2005b)
Modified & unmodified kenaf core, kenaf bast, sugarcane bagasse, cotton, coconut coir, spruce	Ni (II), Cu (II), Zn (II)	Upto88%	Sciban et al. (2007)

Table 6
Summary of work done by various researchers using variety of agricultural waste materials for the removal other metal ions

Agricultural waste	Metal ion	Results	Reference
Chemically treated charred saw dust	As (III), Cr (VI)	80%, 95%	Nag et al. (1998)
Copper impregnated sawdust	As (III)	>99%	Raji and Anirudhan (1998)
Rice husk, Chitini, water hyacinth, cellulose sponge, human hair	As (III)	71–96%	Mohan and Pittman (2007)
Wheat shell	Cu (II)	99%	Basci et al. (2003)
Carbonized corn pith	Cu (II)	90%	
Pinus radiata bark	Multiple metals	>50%	Palma et al. (2003)
Mango saw dust	Cu (II)	60%	Ajmal et al. (1998)
Activated parthenium carbon	Hg (II), Cr (VI), Fe (II)	Significant removal	Rajeshwarisivaraj and Subburam (2002)

5.5. Removal of other metal ions

Other metal ions such as copper, zinc, arsenic, mercury and cobalt present in various industrial effluents are of environmental concern due to their toxicity even in low concentrations. Discharge of these metal ions into the aquatic systems is due to various human and industrial applications (Masri et al., 1974; Prasad and Dubay, 1995). Rice husk and water hyacinth along with other low cost adsorbents were studied for the removal of arsenic and the efficiency varies between 71 and 96% (Mohan et al., 2006b). Variety of agricultural waste viz. parthenium weed, dry pine needles, bamboo pulp, modified cotton fibers and saw dust was utilized for the removal of mercury ions (Masri et al., 1974; Rajeshwarisivaraj and Subburam, 2002; Roberts and Rowland, 1973; Sciban and Klasnja, 2004; Shukla and Sakhardande, 1992). Copper impregnated and chemically modified saw dust was also tried for arsenic removal with significant efficiency. (Nag et al., 1998; Raji and Anirudhan, 1998). Utilization of saw dust also played significant role in removal of copper metal ions (Ajmal et al., 1998; Larous et al., 2005). Other waste materials like wheat shells and carbonized coir pith have shown high efficiency for sequestering copper metal (Basci et al., 2003). Mustard oil cakes and modified bark of pinus radiate have also been proved as potential biosorbent (Ajmal et al., 2005; Palma et al., 2003) (Table 6).

6. Conclusion

Biosorption is a relatively new process that has shown significant contribution for the removal of contaminants from aqueous effluents. In this review the toxic metal ion biosorption on inexpensive and efficient biosorbents from agricultural waste materials have been investigated as replacement strategy for existing conventional systems. The use of these low cost biosorbents is recommended since they are relatively cheap or of no cost, easily available, renewable and show highly affinity for heavy metals. Literature also reveals that in some cases the modification of the adsorbent increased the removal efficiency. However very less work has been carried out in this direction. The process of biosorption requires further investigation in the direction of modeling, regeneration of biosorbent and recovery of metal ions and immobilization of the waste material for enhanced efficiency and recovery. Most of the reported studies are performed in the batch process, this gives a platform for the designing of the continuous flow systems with industrial applications at the commercial level also. Further research is to be carried out to make the process economic viable at industrial scale with focus on metal recovery and regeneration of agricultural waste.

References

Acar, F.N., Malkoc, E., 2004. Removal of Chromium (VI) from aqueous solution by *Fagus orientalis*. Biores. Technol. 94, 13–15.

Ahluwalia, S.S., Goyal, D., 2005a. Removal of heavy metals from waste tea leaves from aqueous solution. Eng. Life Sci. 5, 158–162.

Ahluwalia, S.S., Goyal, D., 2005b. Microbial and plant derived biomass for removal of heavy metals from waste water. Biores. Technol. 98, 2243–2257.

Ajmal, M., Khan, A.H., Ahmed, S., Ahmed, A., 1998. Role of saw dust in the removal of copper (II) from industrial wastes. Water Res. 32, 3085–3091.

Ajmal, M., Rao, R.A.K., Khan, M.A., 2005. Adsorption of Cu from aqueous solution on *Brassica cumpestris* (mustard oil cake). J. Hazard. Mater. B122, 177–183.

Ajmal, M., Rao, R.A.K., Ahmad, R., Khan, M.A., 2006. Adsorption studies on parthenium hysterophrous weed: Removal and recovery of Cd (II) from wastewater. J. Hazard. Mater. B135, 242–248.

Akhtar, N., Iqbal, J., Iqbal, M., 2004. Removal and recovery of nickel (II) from aqueous solution by loofa sponge-immobilized biomass of *Chlorella sorokiniana*: characterization studies. J. Hazard. Mater. B108, 85–94.

Aksu, Z., Acikel, U., Kutsal, T., 1999. Investigation of simultaneous biosorption of copper (II) and chromium (VI) on dried chlorella vulgaris from binary metal mixtures: application of multicomponent adsorption isotherms. Sep. Sci. Technol. 34, 501–524.

Annadurai, G., Juang, R.S., Lee, D.L., 2002. Adsorption of heavy metals from water using banana and orange peels. Water Sci. Technol. 47, 185–190.

Bailey, S.E., Olin, T.J., Bricka, R.M., Adrian, D.D., 1999. A review of potentially low-cost sorbents for heavy metals. Water Res. 33, 2469–2479.

Bankar, D.B., Dara, S.S., 1985. Effectiveness of *Soymida febrifuga* bark for scavenging lead ions. Proc. Nation. Semin. Pollut. Cont. Environ. Manage. 1, 121.

Basci, N., Kocadagistan, E., Kocadagistan, B., 2003. Biosorption of Cu II from aqueous solutions by wheat shells. Desalination 164, 135–140.

Basso, M.C., Cerrella, E.G., Cukierman, A.L., 2002. Lignocellulosic materials as potential biosorbents of trace toxic metals from wastewater. Chem. Res. 41, 3580–3585.

Benaissa, H., 2006. Screening of new sorbent materials for cadmium removal from aqueous solutions. J. Hazard. Mater. 132, 189–195.

Beveridge, T.J., Murray, R.G.E., 1980. Sites of metal deposition in the cell wall of *Bacillus subtilis*. J. Biotechnol. 141, 876–887.

Bishnoi, N.R., Bajaj, M., Sharma, N., Gupta, A., 2004. Adsorption of chromium (VI) on activated rice husk carbon and activated alumina. Biores. Technol. 91, 305–307.

Celik, A., Demirbas, A., 2005. Removal of heavy metal ions from aqueous solutions via adsorption onto modified lignin from pulping wastes. Energy Sources 27, 1167–1177.

Cimino, G., Passerini, A., Toscano, G., 2000. Removal of toxic cations and Cr (VI) from aqueous solution by hazelnut shell. Water Res. 34, 2955–2962.

Dakiky, M., Khamis, M., Manassra, A., Mereb, M., 2002. Selective adsorption of Cr (VI) in industrial wastewater using low cost abundantly available adsorbents. Adv. Environ. Res. 6, 533–540.

Demirbas, A., 2000a. Biomass resources for energy and chemical industry. Energy Edu. Sci. Technol. 5, 21–45.

Demirbas, A., 2000b. Recent advances in biomass conversion technologies. Energy Edu. Sci. Technol 6, 19–40.

Demirbas, E., Kobya, M., Oncel, S., Sencan, S., 2002. Removal of Ni II from aqueous solution by adsorption onto hazelnut shell activated carbon: equilibrium studies. Biores. Technol. 84, 291–293.

Maranon, E., Sastre, H., 1991. Heavy metal removal in packed beds using apple wastes. Biores. Technol. 38, 39–43.

Fahim, N.F., Barsoum, B.N., Eid, A.E., Khalil, M.S., 2006. Removal of Cr (III) from tannery wastewater using activated carbon from sugar industrial waste. J. Hazard. Mater. 136, 303–309.

Farajzadeh, M.A., Monji, A.B., 2004. Adsorption characteristics of wheat bran towards heavy metal cations. Sep. Purif. Technol. 38, 197–207.

Friberg, L., Elinder, C.G., 1985. Encyclopedia of Occupational Health, third ed. International Labor Organization, Geneva.

Friedman, M., Waiss, A.C., 1972. Mercury uptake by selected agricultural products and by-products. Environ. Sci. Technol. 6, 457–458.

Gajghate, D.G., Saxena, E.R., Vittal, M., 1991. Removal of lead from aqueous solution by activated carbon. Ind. J. Environ. Health 33, 374–379.

Gardea-Torresdey, J.L., Tiemann, K.J., Armendariz, V., Bess-Oberto, L., Chianelli, R.R., Rios, J., Parsons, J.G., Gamez, G., 2000. Characterization of chromium (VI) binding and reduction to chromium (III) by the agricultural byproduct of *Avena monida* (oat) biomass. J. Hazard. Mater. B80, 175–188.

Gardea-Torresdey, J.L., Gonzalez, J.H., Tiemann, K.J., Rodriguez, O., Gamez, G., 1998. Phytofilteration of hazardous cadmium, chromium, lead, and zinc ions by biomass of *Medicago sativa* (alfalfa). J. Hazard. Mater. 57, 29–39.

Gardea-Torresdey, J.L., Hejazi, M., Tiemann, K.J., Parsons, J.G., Duarte-Gardea, M., Henning, J., 2002. Use of Hop (*Humulus lupulus*) agricultural by-products for the reduction of aqueous lead (II) environmental health hazards. J. Hazard. Mater. 91, 95–112.

Garg, U.K., Kaur, M.P., Garg, V.K., Sud, D., 2007. Removal of hexavalent Cr from aqueous solutions by agricultural waste biomass. J. Hazard. Mater. 140, 60–68.

Garg, U.K., Kaur, M.P., Garg, V.K., Sud, D., in press. Removal of Ni (II) from aqueous solution by adsorption on agricultural waste biomass using a response surface methodological approach. Biores. Technol.

Garg, V.K., Gupta, R., Kumar, R., Gupta, R.K., 2004. Adsorption of chromium from aqueous solution on treated sawdust. Biores. Technol. 92, 79–81.

Gupta, V.K., Ali, I., 2000. Utilization of bagasse fly ash (a sugar industry waste) for the removal of copper and zinc from wastewater. Separation and Purification Technol. 18, 131–140.

Gupta, V.K., Ali, I., 2004. Removal of lead and chromium from wastewater using bagasse fly ash – a sugar industry waste. J. Colloid Interface Sci. 271, 321–328.

Gupta, V.K., Jain, C.K., Ali, I., Sharma, M., Saini, V.K., 2003. Removal of cadmium and nickel from wastewater using bagasse fly ash- a sugar industry waste. Water Search 37, 4038–4044.

Gupta, V.K., Mohan, D., Sharma, S., Park, K.T., 1999. Removal of Cr VI from electroplating industry wastewater using bagasse fly ash. The Environmentalist 19, 129–136.

Hanif, M.A., Nadeem, R., Zafar, M.N., Akhtar, K., Bhatti, H.N., 2007. Nickel (II) biosorption by *Casia fistula* biomass. J. Hazard. Mater. B139, 345–355.

Hashem, A., Abdel-Halim, E.S., El-Tahlawy, K.F., Hebeish, A., 2005a. Enhancement of adsorption of Co (II) and Ni (II) ions onto peanut hulls though esterification using citric acid. Adsorp. Sci. Technol. 23, 367–380.

Hashem, A., Akasha, R.A., Ghith, A., Hussein, D.A., 2005b. Adsorbent based on agricultural wastes for heavy metal and dye removal: A review. Energy Edu. Sci. Technol. 19, 69–86.

Hashem, A., Abou-Okeil, A., El-Shafie, A., El-Sakhawy, M., 2006a. Grafting of high-cellulose pulp extracted from sunflower stalks for removal of Hg (II) from aqueous solution. Polym.-Plast. Technol. Eng. 45, 135–141.

Hashem, A., Aly, A.A., Aly, A.S., Hebeish, A., 2006b. Quaternization of cotton stalks and palm tree particles for removal of acid dye from aqueous solutions. Polym.-Plast. Technol. Eng. 45, 389–394.

Haung, C., Haung, C.P., 1996. Application of *Aspergillus oryzae* and *Rhizopus oryzae* for Cu (II) removal. Water Res. 9, 1985–1990.

Ho, Y.S., Mckay, G., 1998. The kinetics of sorption of basic dyes from aqueous solution by sphagnum moss peat. Can. J. Chem. Eng. 76, 822–827.

Ho, Y., Huang, C.T., Haung, H.W., 2002. Equilibrium sorption isotherm for metal ions on tree fern. Process Biochem. 37, 1421–1430.

Horikoshi, T., Nakajima, A., Sakaguchi, T., 1981. Studies on the accumulation of heavy metal elements in biological systems, XIX: accumulation of uranium by microorganisms. Eur. J. Appl. Microbiol. Biotechnol. 12, 90–96.

Hosea, M., Greene, B., McPherson, R., Henzl, M., Alexander, M.D., Darnall, D.W., 1986. Accumulation of elemental gold on alga *Chlorella vulgaris*. Inorg. Chim. Acta 123, 161–165.

Iqbal, M., Saeed, A., Akhtar, N., 2002. Petiolar felt sheet of palm: a new biosorbent for the removal of heavy metals from contaminated water. Biores. Technol. 81, 151–153.

Iqbal, M., Saeed, A., Akhtar, N., 2005. Removal and recovery of lead II from single and multiple (Cd, Cu, Ni, Zn) solutions by crop milling waste (black gram husk). J. Hazard. Mater. 117, 65–73.

Johns, M.M., Marshall, W.E., Toles, C.A., 1998. Agricultural byproducts as granular activated carbons for adsorbing dissolved metals and organics. J. Chem. Technol. Biotechnol. 71, 131–140.

Kadirvelu, K., Namasivayam, C., Thamaraiselve, K., 2001. Removal of heavy metal from industrial wastewaters by adsorption on to activated carbon prepared from an agricultural solid waste. Biores. Technol. 76, 63–65.

Kamble, S.K., Patil, M.R., 2001. Removal of heavy metals from waste water of thermal power station by water-hyacinths. Ind. J. Environ. Protect. 21, 623–626.

Kannan, N., Rengasamy, G., 2005. Comparison of Cd adsorption on various activated carbon. Water Air Soil Pollut. 163, 185–201.

Karthikeyan, T., Rajgopal, S., Miranda, L.R., 2005. Cr (VI) adsorption from aqueous solution by *Hevea brasilinesis* saw dust activated carbon. J. Hazard. Mater. 124, 192–199.

Karnitz Jr., O., Gurgel, L.V.A., Melo, J.C.P., Botaro, V.R., Melo, T.M.S., Gil, R.P.F., Gil, L.F., 2007. Adsorption of heavy metal ion from aqueous single metal solution by chemically modified sugarcane bagasse. Biores. Technol. 98, 1291–1297.

Kjellstrom, T., Shiroishi, K., Erwin, P.E., 1977. Urinary beta./sub 2/-microglobulin excretion among people exposed to cadmium in the general environment. Environ. Res. 13, 318–344.

Krishanani, K.K., Parmila, V., Meng, X., 2004. Detoxification of chromium (VI) in coastal water using lignocellulosic agricultural waste. Water SA. 30, 541–545.

Krishnan, K.A., Anirudhan, T.S., 2003. Removal of cadmium (II) from aqueous solutions by steam-activated sulphurised carbon prepared

from sugar cane bagasse pith: Kinetics and equilibrium studies. Water SA. 29, 147–156.
Kumar, U., Bandyopadhyay, M., 2006. Sorption of Cd from aqueous solution using pretreated rice husk. Biores. Technol. 97, 104–109.
Kurniawan, T.A., Chan, G.Y.S., Lo, W.H., Babel, S., 2006. Comparison of low-cost adsorbents for treating wastewater laden with heavy metals. Sci. Total Environ. 366, 409–426.
Larous, S., Meniai, A.H., Lehocine, M.B., 2005. Experimental study of the removal of Cu from the aqueous solutions by adsorption using saw dust. Desalination 185, 483–490.
Lee, S.H., Shon, J.S., Chung, H.S., Lee, M.Y., Yang, J.W., 1999. Effect of chemical modification of carboxyl groups in apple residues on metal ion binding. Kor. J. Chem. Eng. 16, 576–580.
Macchi, G., Marani, D., Tirivanti, G., 1986. Uptake of mercury by exhausted coffee grounds. Environ. Technol. Lett. 7, 431–444.
Malkoc, E., Nuhoglu, Y., 2005. Investigation of Ni II removal from aqueous solutions using tea factory waste. J. Hazard. Mater. B127, 120–128.
Manju, G.N., Anirudhan, T.S., 1997. Use of coconut fiber pith-based pseudo activated carbon for chromium (VI) removal. Ind. J. Environ. Health 4, 289–298.
Marshall, W.E., Johns, M.M., 1996. Agricultural by products as metal adsorbents: sorption properties and resistance to mechanical abrasion. J. Chem. Tech. Biotechnol. 66, 192–198.
Masri, M.S., Reuter, F.W., Friedman, M., 1974. Binding of metal cations by natural substances. J. Appl. Polym. Sci. 18, 675–681.
Mehrotra, R., Dwivedi, N.N., 1988. Removal of chromium (VI) from water using unconventional materials. J. Ind. Water Works Assoc. 20, 323–327.
Min, S.H., Han, J.S., Shin, E.W., Park, J.K., 2004. Improvement of cadmium ion removal by base treated juniper fiber. Water Res. 38, 1289–1295.
Mohan, D., Pittman, C.U., 2007. Arsenic removal from water/wastewater using adsorbents – a critical review. J. Hazard. Mater. 142, 1–53.
Mohan, D., Singh, K.P., 2002. Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse-an agricultural waste. Water Res. 36, 2304–2318.
Mohan, D., Singh, K.P., Singh, V.K., 2006a. Chromium (III) removal from wastewater using low cost activated carbon derived from agriculture waste material and activated carbon fabric filter. J. Hazard. Mater. B135, 280–295.
Mohan, D., Singh, K.P., Singh, V.K., 2006b. Trivalent Cr removal from wastewater using low cost activated carbon derived from agricultural waste material and activated carbon fabric cloth. J. Hazard Mater. B135, 280–295.
Mohanty, K., Jha, M., Biswas, M.N., Meikap, B.C., 2005. Removal of chromium (VI) from dilute aqueous solutions by activated carbon developed from *Terminalia arjuna* nuts activated with zinc chloride. Chem. Eng. Sci. 60, 3049–3059.
Montanher, S.F., Oliveira, E.A., Rollemberg, M.C., 2005. Removal of metal ions from aqueous solutions by sorption onto rice bran. J. Hazard. Mater. B 117, 207–211.
Nag, A., Gupta, N., Biswas, M.N., 1998. Removal of chromium (VI) and arsenic (III) by chemically treated saw dust. Ind. J. Environ. Protect. 19, 25–29.
Nasir, M.H., Nadeem, R., Akhtar, K., Hanif, M.A., Khalid, A.M., 2007. Efficacy of modified distillation sludge of rose (*Rosa centifolia*) petals for lead and zinc removal from aqueous solutions. J. Hazard. Mater. 147, 1006–1014.
Oliveira, E.A., Montanher, S.F., Andnade, A.D., Nobrega, J.A., Rollemberg, M.C., 2005. Equilibrium studies for the sorption of chromium and nickel from aqueous solutions using raw rice bran. Process Biochem. 40, 3485–3490.
Orhan, Y., Bujukgungor, H., 1993. The removal of heavy metals by using agricultural wastes. Water Sci. Technol. 28, 247–255.
Palma, G., Freer, G.J., Beeza, J., 2003. Removal of metal ions by modified *Pinus radiata* bark and tannins from water solutions. Water Res. 37, 4974–4980.
Park, D., Yun, Y.S., Lim, S.R., Park, J.M., 2006. Kinetic analysis and mathematical modeling of Cr (VI) removal in a differential reactor packed with ecklonia biomass. J. Microbiol. Biotechnol. 16, 1720–1727.
Pastircakova, K., 2004. Determination of trace metal concentrations in ashes from various biomass materials. Energy Edu. Sci. Technol. 13, 97–104.
Patterson, J.W., 1985. Industrial Wastewater Treatment Technology, second ed. Butterorth Publisher, Stoneham, MA.
Pino, G., de Mesquita, L., Torem, M., Pinto, G., 2006. Biosorption of heavy metals by powder of green coconut shell. Sep. Sci. Technol. 41, 3141–3153.
Prasad, S.C., Dubay, R.B., 1995. Arsenic (III) removal by sorption on coconut shell. Ind. J. Environ. 75, 36–47.
Qaiser, S., Saleemi, A.R., Ahmad, M.M., 2007. Heavy metal uptake by agro based waste materials. Environ. Biotechnol. 10, 409–416.
Rajeshwarisivaraj, Subburam, V., 2002. Activated parthenium carbon as an adsorbent for the removal of dyes and heavy metal ions from aqueous solution. Biores. Technol. 85, 205–206.
Raji, A.K., Anirudhan, T.S., 1998. Sorptive behaviour of chromium (VI) on saw dust carbon in aqueous media. Ecol. Environ. Conserv. 4, 33–37.
Raji, C., Shubha, K.P., Anirudhan, T.S., 1997. Use of chemically modified sawdust in the removal of Pb (II) ions from aqueous media. Ind. J. Environ. Health 39, 230–238.
Rao, M., Parwate, A.V., 2002. Utilization of low-cost adsorbents for the removal of heavy metals from wastewater – a review. J. Environ. Pollut. Control 5, 12–23.
Rao, M., Parwate, A.V., Bhole, A.G., 2002. Removal of Cr and Ni from aqueous solution using bagasse and fly ash. Waste Manage. 22, 821–830.
Randall, J.M., Hautala, E., Waiss, Jr. A.C., 1974. Removal and recycling of heavy metal ions from mining and industrial waste streams with agricultutral by-products. In: Proceedings of the Fourth Mineral Waste Utilization Symposium. Chicago.
Reddad, Z., Gerente, C., Andres, Y., Ralet, M.-C., Thibault, J.-F., Cloirec, P.L., 2002. Ni (II) and Cu (II) binding properties of native and modified sugar beet pulp. Carbohydr. Polym. 49, 23–31.
Roberts, E.J., Rowland, S.P., 1973. Removal of mercury from aqueous solutions by nitrogen-containing chemically modified cotton. Environ. Sci. Technol. 7, 552–555.
Saeed, A., Akhter, M.W., Iqbal, M., 2005a. Removal and recovery of heavy metals from aqueous solution using papaya wood as a new biosorbents. Sep. Purif. Technol. 45, 25–31.
Saeed, A., Iqbal, M., Akhtar, M.W., 2005b. Removal and recovery of lead (II) from single and multiple, (Cd, Ni, Cu, Zn) solutions by crop milling waste (black gram husk). J. Hazard. Mater. 117, 65–73.
Saeed, A., Iqbal, M., 2003. Bioremoval of Cd from aqueous solution by black gram husk (*Cicer arientinum*). Water Res. 37, 3472–3480.
Sarin, V., Pant, K.K., 2006. Removal of chromium from industrial waste by using eucalyptus bark. Biores. Technol. 97, 15–20.
Sarkanen, K.V., Ludwig, C.H., 1971. Lignins-Occurance, Formation, Structure and Reactions. Wiley-Interscience, New York, 1.
Sciban, M., Klasnja, M., 2004. Wood saw dust and wood originate materials as adsorbents for heavy metal ions. Holz Roh Werkst. 62, 69–73.
Sciban, M., Radetic, B., Kevresan, Z., Klasnja, M., 2007. Adsorption of heavy metals from electroplating waste water by wood saw dust. Biores. Technol. 98, 402–409.
Sciban, M., Klasnja, M., Skrbic, B., 2006. Modified hardwood sawdust as adsorbent of heavy metal ions from water. Wood Sci. Technol. 40, 217–227.
Seki, K., Saito, N., Aoyama, M., 1997. Removal if heavy metal ions from solutions by coniferous barks. Wood Sci. Technol. 31, 441–447.
Shukla, S.R., Pai, R.S., 2005. Adsorption of Cu (II), Ni (II) and Zn (II) on modified jute fibres. Biores. Technol. 96, 1430–1438.
Shukla, S.R., Sakhardande, V.D., 1992. Column studies on metal ion removal by dyed cellulosic materials. J. Appl. Polym. Sci. 44, 903–910.

Shukla, S.S., Yu, L.J., Dorris, K., Shukla, A., 2005. Removal of nickel from aqueous solutions by saw dust. J. Hazard. Mater. B121, 243–246.

Singh, K.K., Rastogi, R., Hasan, S.H., 2005. Removal of cadmium from waste water using agricultural waste using rice polish. J. Hazard. Mater. A121, 51–58.

Sjötröm, E., 1981. Wood Chemistry Fundamentals and Applications. Academic Press Inc., New York.

Srinivasan, K., Balasubramanian, N., Ramakrishnan, T.V., 1988. Studies on chromium removal by rice husk carbon. Ind. J. Environ. Health 30, 376–387.

Srivastava, S., Ahmed, A.H., Thakur, I.S., 2007. Removal of chromium and pentachlorophenol from tannery effluent. Biores. Technol. 98, 1128–1132.

Srivastva, S.K., Gupta, V.K., Mohan, D., 1996. Kinetic parameters for the removal of lead and chromium from waste water using activated carbon developed fertilizer waste material. Environ. Model. Assess. 1, 281–290.

Sudha, B.R., Abraham, E., 2003. Studies on chromium (VI) adsorption using immobilized fungal biomass. Biores. Technol. 87, 17–26.

Tarley, C.R.T., Arruda, M.A.Z., 2004. Biosorption of heavy metals using rice milling byproducts. Characterization and application for removal of metals from aqueous effluents. Chemosphere 54, 987–995.

Taty-Costodes, V.C., Favdvet, H., Porte, C., Delacroix, A., 2003. Removal of cadmium and lead ions from aqueous solutions, by adsorption onto saw dust of *Pinus sylvestris*. J. Hazard. Mater. B105, 121–142.

Tee, T.W., Khan, R.M., 1988. Removal of lead, cadmium and zinc by waste tea leaves. Environ. Technol. Lett. 9, 1223–1232.

Tsui, M.T.K., Cheung, K.C., Tam, N.F.Y., Wong, M.H., 2006. A comparative study on metal sorption by brown seaweed. Chemosphere 65, 51–57.

Valix, M., Cheung, W.H., Zhang, K., 2006. Role of heteroatom in activated carbon for the removal of hexavalent Cr from wastewater. J. Hazard. Mater. 135, 395–405.

Vaughan, T., Seo, C.W., Marshall, W.E., 2001. Removal of selected metal ions from aqueous solutions using modified corncobs. Biores. Technol. 78, 133–139.

Venkateswarlu, P., Ratnam, M.V., Rao, D.S., Rao, M.V., 2007. Removal of chromium from aqueous solution using *Azadirachta indica* (neem) leaf powder as an adsorbent. Int. J. Phys. Sci. 2, 188–195.

Vieira, R.H.S.F., Volesky, B., 2000. Biosorption: a solution to pollution. Int. Microbiol. 3, 17–24.

Volesky, B., Holan, Z.R., 1995. Biosorption of heavy metals. Biotechnol. Progr. 11, 235–250.

Wafwoy, W., Seo, C.W., Marshall, W.E., 1999. Utilization of peanut shells as adsorbents for selected metals. J. Chem. Technol. Biotechnol. 74, 1117–1121.

Wilson, W., Yang, H., Seo, C.W., Marshall, W.E., 2006. Select metal adsorption by activated carbon made from peanut shells. Biores. Technol. 97, 2266–2270.

Yu, B., Zhang, Y., Shukla, S.S., Dorris, K.L., 2000. The removal of heavy metal from aqueous solutions by sawdust adsorption – removal of copper. J. Hazard. Mater. B 80, 33–42.

Yu, B., Zhang, Y., Shukla, A., Shukla, S., Dorris, K.L., 2001. The removal of heavy metals from aqueous solutions by sawdust adsorption–removal of lead and comparison of its adsorption with koper. J. Hazard. Mater. 84, 83–94.

Zhang, L., Zhao, L., Yu, Y., Chen, C., 1998. Removal of lead from aqueous solution by non-living *Rhizopus nigricans*. Water Res. 32, 1437–1444.

Zhou, J.L., Kiff, R.J., 1991. The uptake of copper from aqueous solution by immobilized fungal biomass. J. Chem. Technol. 52, 317–330.

Zulkali, M.M.D., Ahmed, A.C., Norulakmal, N.H., 2006. *Oriza sativa* husk as heavy metal adsorbent: optimization with lead as model solution. Biores. Technol. 97, 21–25.