Journal of Environment & Biotechnology Research
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Lignocellulosic biosorbents for the removal of hexavalent chromium from aqueous solutions: A review

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REVIEW ARTICLE

ABSTRACT

Hexavalent chromium is a highly toxic metal which has its sources from the industrial sectors of leather tanning, mining of chrome ore, electroplating, anodizing baths, production of steel and alloys, rinse waters, etc. Biosorption of hexavalent chromium using lignocellulosic biomass has been identified as an alternative approach to the conventional technologies. This article deals with the survey on utilization of natural and modified forms of lignocellulosic biomass for the removal of hexavalent chromium. The potential of various lignocellulosic biomasses for the hexavalent chromium removal was reported on the basis of the biosorption capacity. The methods for the preparation of the natural and modified form of lignocellulosic biomass towards hexavalent chromium removal were outlined. The study demonstrated that the waste biomass can be utilized as an economical and eco-friendly biosorbent for the removal of hexavalent chromium from aqueous solutions.

KEYWORDS

biosorption capacity; hexavalent chromium; lignocellulosic biomass; low cost biosorbents; metal toxicity

1. INTRODUCTION

Heavy metal contamination is nowadays a major threat to the environment due to the increasing industrialization. Heavy metals are highly toxic, non-biodegradable and have various health effects on humans (Pellerin and Booker, 2000). Chromium is one of the toxic heavy metal and listed in the top 20 hazardous substances for the past 15 years. Chromium find its industrial applications in leather tanning, metal corrosion inhibition, steel production, wood preservation, inks, glass, ceramics, paint and pigments, metal plating and certain glues. Chromium occurs in the aqueous solution with two different oxidation states such as trivalent chromium and hexavalent chromium (Namasivayam and Ranganathan, 1993; Chrysochoou and Johnston, 2012). Hexavalent chromium is 500 times more toxic than trivalent chromium. Hexavalent chromium is mobile in the environment and carcinogenic, mutagenic to living organisms. The toxicity effects of hexavalent chromium include nausea, diarrhea, pulmonary congestion, liver damage, skin irritation, ulcer formation, nerve tissue damage, internal hemorrhage etc. Whereas, trivalent chromium at lower concentration is essential to the living systems and has significant role in the metabolism of sugar and fat (Kowalski, 1994; Kotas and Stasicka, 2000; Dinesh and Charles, 2006). The guideline value for chromium on the basis of an inorganic constituent of health importance is about 0.05 mg/L. According to Environmental Protection Agency, the maximum permissible level for hexavalent chromium in the drinking water is 0.1 mg/L (Haq et al., 2010). Therefore, it is desirable to remove hexavalent chromium from the industrial effluent before discharged into the environment.

Several conventional methods like ion exchange, electrochemical precipitation, solvent extraction,

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Received: 11-09-2016
Revised: 16-09-2016
Accepted: 23-09-2016
Available online: 01-10-2016

evaporation, reverse osmosis, membrane separation, foam separation and adsorption by activated carbon were available for decontamination of metals from wastewaters. However, generation of toxic by-products, high requirement of energy and chemical, incomplete metal removal process and ineffectiveness at low concentration limits these conventional techniques from their usage in larger applications (Crini, 2006; Gupta and Babu, 2009; Bhatnagar and Sillanpa, 2010).

2. BIOSORPTION PROCESS

In comparison to the conventional methods, biosorption is a simple physicochemical process which uses materials of biological origin. The process is cost-effective, efficient and the biosorbent are biodegradable in nature, and thus can be an alternative solution for the removal of heavy metal from the aqueous solution. Recently, applying the biosorption process for the toxic heavy metal removal has been explored by several researchers for preparation of novel biosorbents (Vijayaraghavan et al, 2016; Rangabhashiyam et al, 2014a). Biosorption process is a growth independent process, which employs inactive biomass as an ion exchanger. The process takes place between few minutes to hours, free from the requirement of aseptic condition and formation of sludge. Biosorption process can be operated by adjusting several operating parameter conditions such as solution pH, biosorbent dosage, initial metal ion concentration, and temperature, etc. After biosorption process, the biosorbent can be separated from the bounded toxic heavy metal ions through desorption process. Based on the availability of the biosorbent, it can be either reused for further metal removal process or left to environment as it is biodegradable in nature (Sarabjeet and Dinesh, 2007; Rangabhashiyam et al. 2014b; Rangabhashiyam et al. 2016).

3. LIGNOCELLULOSE AND ITS MAJOR CONSTITUENTS

The main sources of the lignocellulosic biomass are from the agricultural and natural plant wastes. Lignocellulosic biomass are available in copiousness and the cost of the biomass is cheap or even available at free of cost. These are main factors for choosing lignocellulosic biomass in metal removal rather than using high cost commercial activated carbon (Malik at al., 2016). The main constituents of the plant biomass include cellulose, hemicelluloses, lignin, as well contain various functional groups such as carboxyl, hydroxyl, sulfate, amino groups, alcohols, aldehydes, ketones, carboxylates phenols and ethers. These functional groups play a key role in binding toxic heavy metals through hydrogen ion replacement with metal ions in solution or through electron pair donation from these functional groups to form metal ions complexes. The characteristics of the biomass, physico-chemical properties of the toxic heavy metal and solution pH are the important controlling factors of the biosorption performance (Rao et al, 2005; Ofomaja and Ho, 2007). Cellulose is a linear polymer of β–(1,4) linked glucose units and the average chain of the cellulose has a degree of polymerization of about 9000 to 10,000 units. Cellulose is present in plant cell in combination with lignin and hemicellulose. The glucose residues containing hydroxyl groups of one chain forms hydrogen bonds with oxygen present on another chain. The cellulose tends to be aggregated together in such a way to form microfibrils in highly ordered crystalline regions and less ordered amorphous regions. In most of the solvents, the cellulose was found to be insoluble and it has low accessibility towards the hydrolysis of acid and enzyme. Hemicellulose is another important constituent of the plant biomass, which is formed by a group of polysaccharides. Hemicelluloses are not crystalline in structure and composed of different monomer units, out of which glucose and xylose are mainly present, then xylose, mannose, galactose, rhamnose, arabinose, and glucuronic acids are also distributed in its structure (Celik and Demirbas, 2005; Cagnon et al., 2009).

Lignin are highly branched polymer consists of alkylphenols. Lignin fills the spaces in the cell wall region between cellulose, hemicellulose and pectin, providing mechanical strength to the cell wall structure. In the plants cell wall, lignin is the second abundant component next to the cellulose. Lignin is an amorphous cross linked resin which acts as the chief binder for agglomeration of fibrous cellulosic components. Lignin is covalently linked with xylans in the hardwoods and with galactoglucomannans in the softwoods. The basic structural lignin units are held together through linkages and thereby form a very complex matrix. The presence of hydroxyl, methoxyl and carbonyl functional groups are responsible for the high polar nature of lignin macromolecule (Hashem et al., 2007; Guo et al., 2008).

4. BIOSORPTION PROCESS

Several studies have been reported on the use of various agricultural waste and by-products, natural plant waste biomass for the removal of hexavalent chromium from the aqueous solutions. Few examples of best performed lignocellulosic biomasses towards hexavalent chromium removal are hazelnut shell (Kobya, 2004), rice bran (Singh et al. 2005), sunflower stem waste (Jain et al. 2009), eucalyptus bark (Sarin and Pant, 2006), pine needles, olive cake, wool, almond, soya cake (Dakiky et al. 2002), sugarcane bagasse (Wartelle and Marshall, 2005), Bengal gram husk (Ahalya et al. 2005), coconut husk fibers, *Ocimum basilicum* seeds (Melo and Souza, 2004), cactus (Dakiky et al., 2002), walnut shell (Pehlivan and Altun, 2008), persimmon waste (Katsutoshi et al., 2010), olive pomace (Krishnani et al., 2008), *Melaleuca diosmifolia* leaf (Saranya et al., 2016), palm flower (Elangovan et al., 2008a), groundnut husk (Shashi and Krishna, 2007), *Araucaria* leaves (Dhara and Padma, 2012), sawdust (Saroj et al., 2006), *Pinus densiflora* leaves (Donghee et al., 2011), *Leersia hexandra* Swartz biomass (Li et al., 2009), etc. Every lignocellulosic biomass comprises of desirable characteristics, structural compounds with distinct chemical functional groups to adsorb hexavalent chromium on its surface. The sequestration of hexavalent chromium by lignocellulosic biomass can be accomplished through natural form (without modification) and by means of activated form (with modification). Based on the biomass nature of lignocellulose, the performance towards the metal removal varies. In the present study the potential of various natural and activated lignocellulosic biomasses were analysed on the basis of biosorption capacity towards the hexavalent chromium removal. Figure 1 illustrates the use of raw and modified form of lignocellulosic biosorbent and their assessment through adsorption capacity for the removal of hexavalent chromium from aqueous solution.

4.1. The natural form of lignocellulosic biomass for Cr(VI) biosorption

A wide variety of plant biomasses has been explored in the raw form for the hexavalent chromium biosorption. In those cases of natural form of biomass without any pre-treatment, the collected waste or by-product lignocellulose biomass usually washed thoroughly using distilled water in order to remove the soluble impurities and further dried in the hot oven. The resulted dried biosorbent generally be grounded using a blender and subsequently sieved for the desired particle size range. The resultant lignocellulosic biosorbent employed for metal removal without any additional treatment (Xue et al., 2009). The maximum biosorption capacities of different types of agricultural waste, by-products and

Table 1. The biosorption capacities of natural lignocellulosic biosorbents for the removal of hexavalent chromium from aqueous solutions.

Biosorbent	Biosorption capacity (mg/g)	Reference
Rice husk	8.5	Bansal et al. 2009
Caryota urens inflorescence	100.0	Rangabhashiyam and Selvaraju, 2015a
Sal sawdust	9.55	Saroj et al., 2006
Beech sawdust	16.1	Karthikeyan et al., 2005
Japanese cedar	71.9	Aoyama et al., 2005
Coconut coir	6.30	Gonzalez et al., 2008
Mangrove leaves	8.87	Elangovan et al., 2008b
Cactus	7.08	Dakiky et al., 2002
Ficus auriculata leaves powder	13.3	Rangabhashiyam et al., 2015b
Eichhornia crassipes	5.6	Saraswat and Rai, 2010
Sterculia guttata shell	45.5	Rangabhashiyam et al., 2015c
Mangifera indica sawdust	12.8	Kapur and Mondal, 2013
Swietenia mahagoni shell	37.0	Rangabhashiyam et al., 2015d
Carrot waste	88.3	Haq et al., 2010
Ficus glomerata	46.7	Rifaqat and Fouzia, 2010
Melaleuca diosmifolia leaf	62.5	Saranya et al., 2016

plant waste biomass biosorbents used in the natural form for the removal of hexavalent chromium are summarized in Table 1. In earlier research (Gupta et al., 2013a), the biomass of *Ficus carica* bark was washed with double distilled water to get rid of the dirts, then soaked in water until the fiber was separated from the gummy substances. Further the fiber material washed using solution of detergent, rinsed with double-distilled and then air dried. In order to remove the adhering organic particles, the fibers were subjected to Soxhlet extraction process with acetone and then dried in a vacuum oven. The biomass sieved for the size range of 1.0-1.5 mm and finally stored in desiccators (Gupta et al., 2013a). In another study (Gebrehawaria et al., 2015), the biosorbents from the barks of *Acacia albida* and *Euclea schimperi* leaves were prepared by cutting the collected biomass into small pieces, sun light dried for about 2 days. The dried biomass sieved in the size range of 0.710 - 1.0 mm. The prepared biosorbents preserved in the air tight plastic bottles (Gebrehawaria et al., 2015).

The waste cone biomass of *Pinus sylvestris* Linn., was dried at 80 °C for 24 h after thorough washing with distilled water, ground in a mortar and sieved through a 400-mesh sieve (Handan et al., 2008). The fresh *Eichhornia crassipes was* washed with water to remove dirt and placed the cleaned biomass on the filter paper to remove the water content. Then the biomass was sun dried for 1 day and dried at 60°C for the time duration of 2 h. The dried biomass reduced to powder form using ball mill and screened to the mesh size of 52 (Kaustubha et al., 2006). Rangabhashiyam and Selvaraju (2015a) washed *Caryota urens* inflorescence waste biomass using distilled water and dried in hot air oven. The dried biomass was then grounded using blender and sieved to obtain the biosorbent particles in three different size ranges of <0.425, 0.425–0.5 and 0.5–0.6 mm. Umesh et al. (2007) dried sugarcane bagasse in sun light and pith was separated. Subsequently, it was boiled with distilled water to remove the soluble sugars in it. Then the biomass was dried and sieved for 150 µm size. Maize corncobs biomass was boiled first with distilled water, dried in hot air oven and sieved to the size of 150 µm. Jatropha oil cakes biosorbent from Jatropha processing industry prepared by hot air oven drying, ground and sieved to obtain the size of 150 µm (Umesh et al., 2007). Leaves of *Ficus auriculata* biomass washed with double distilled water in order to remove sand particles and debris. Then the biomass was air dried for 3 days and then oven dried. The biomass was then cut into small pieces, grounded using blender, and passed through a 140-mesh size (Rangabhashiyam and Selvaraju, 2015b). The biomass portions of stem and leaves of *Portulaca oleracea* was washed with de-ionized water, sun-dried for about 10 days, and then dried in microwave for about 30 min. The dried biomass was then ground and sieved to get the different size particles of 200 -1000 µm (Mishra et al., 2015).

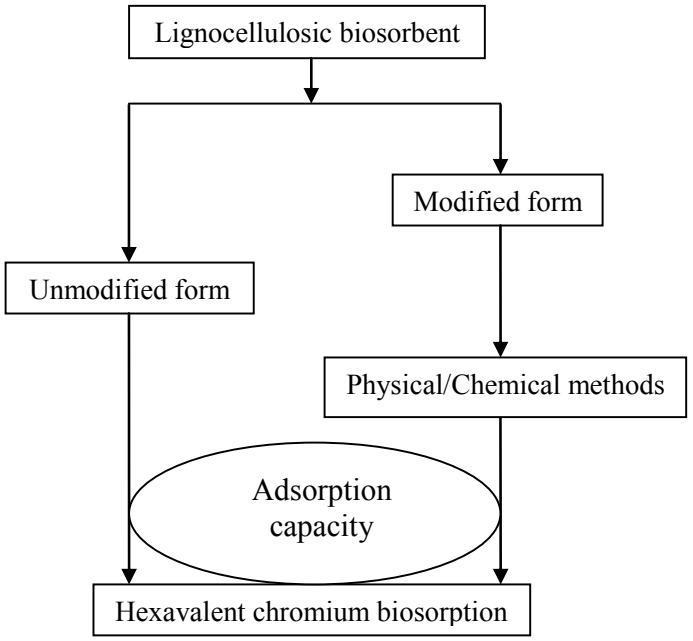

Figure 1. Schematic diagram for the use of lignocellulosic biosorbent towards the removal of hexavalent chromium.

4.2. The modified form of lignocellulosic biomass towards Cr(VI) removal

Apart from the usage of natural form of lignocellulosic biomass towards hexavalent chromium, many pre-treatment methods were available for adsorbent preparation from lignocellulosic biomass for the removal of hexavalent chromium. The modification of the biomass performed through the carbonization of the natural biomass, followed with the activation of the carbonized material through physical or chemical methods (Ioannidou and Zabaniotou, 2007). The physical method of activation performed through the carbonization of biomass at high temperature so that the volatile content present in the biomass can be eliminated. Then the material subjected to the partial gasification using mild oxidizing agents, which generates high porosity and larger surface area to the

biomass. The chemical activation of the biomass usually performed using various chemical agents such as zinc chloride, phosphoric acid, sulfuric acid, hydrochloric acid, tartaric acid, citric acid, nitric acid, etc. These chemical agents remove the soluble organic compounds in biomass, eliminate colouration in the aqueous solutions and increases efficiency of the adsorption of the metal. The fundamental difference between physical and chemical method of biomass activation is the number of stages required for activation and the activation temperature (Ngah and Hanafiah, 2008; Dinesh and Charles, 2006). The adsorption capacities of various activated biomasses towards the hexavalent chromium removal are presented in Table 2.

Rangabhashiyam et al. (2015d) initially modified Swietenia mahagoni shell using sulfuric acid (biomass: acid ratio, 1:2 w/v), and then allowed to carbonize at temperature of 150 °C in hot air oven for 24 h. The carbonized material washed using distilled water and further soaked in 1% sodium bicarbonate solution to remove any remaining sulfuric acid. The obtained carbon finally washed with distilled water and dried at 105 °C for 24 h. Using the same biomass another type of modification was performed using ortho-phosphoric acid (biomass:acid ratio, 1:2.5 w/v). After acid treatment, the sample was dried at 110 °C for 2–3 h. Then the sample was carbonized in muffle furnace up to 400 °C, with the time duration of 1.5 h. To prevent any residual acid effect on the adsorbent, 1% sodium bicarbonate solution was used. Then again the material washed with distilled water and dried at 105 °C for 24 h (Rangabhashiyam et al., 2015d). After washing and drying the seeds of tamarind, they were crushed using jaw crusher and sieved in the mesh screens of 10–12. The average particles size of 1.85 mm biomass were treated with concentrated sulfuric acid in the weight ratio of 1:1, at 150 °C for 24 h. The carbonized material washed with distilled water and then soaked in 1% sodium bicarbonate solution. A final wash with distilled water was performed and again oven dried at 100 °C for 5 h (Gupta and Babu, 2009). *Terminalia arjuna* nuts were washed with distilled water and then hot air oven dried. The dried biomass was grounded using ball mill and sieved to the desired size range. Activation performed using the chemical agent of $ZnCl_2$. The chemical ratio of activating agent to the biomass was about 100%. The $ZnCl_2$ mixed biomass was carbonized in a tubular reactor by heating at 5 °C/min under the supply of nitrogen flow rate 150 mL/min at standard temperature and pressure. Nitrogen was first preheated in the temperature range of 250–300 °C and then passed to the tubular reactor. The material then washed with 0.5 N HCl, hot water and finally using cold distilled water in such a way to eliminate the residual organic and mineral matters. Then the prepared material was dried at 110 °C (Kaustubha et al., 2005).

The cleaned, sieved and crushed peanut shells treated with 20% KOH solution (1:1 w/w), allowed to remain in contact for 24 h at room temperature. The

Table 2. The modified form of lignocellulosic biomasses and their adsorption capacities towards hexavalent chromium removal.

Activated biomass	Adsorption capacities (mg/g)	References
Pomegranate husk	35.2	Ahmed, 2009
Tamarind seeds	29.7	Gupta and Babu, 2009
Ficus carica fiber	44.84	Gupta et al., 2013
Sesame stems	189.1	Veyis et al., 2014
Longan seed	35.02	Jinbei et al., 2015
Peanut shell	16.26	Al-Othman., 2012
Tamarind wood	28.019	Jyotikusum et al., 2009
Terminalia arjuna nuts	28.43	Kaustubha et al., 2005
Eichhornia crassipes root	36.34	Anil et al., 2012
Eupatorium adenophorum and Buckwheat straw	55.19	Jinfa et al., 2014
Sterculia guttata shell	90.90	Rangabhashiyam et al., 2015c
Swietenia mahagoni shell	47.61	Rangabhashiyam et al., 2015d
Sawdust	9.55	Baral et al., 2006
Bael fruit shell	17.27	Anandkumar and Mandal, 2009
Olive bagasse	88.59	Demiral et al., 2008

KOH treated biomass of 25 g was carbonized by placing it in a horizontal tube furnace. During the carbonization process, the temperature raised from room to 170 °C (±5 °C) for 1 h and at 450 °C (±5 °C) for another 1 h under the nitrogen supply at the flow rate of 100 mL/min. The one-half of the prepared sample was oxidized through breathing grade air with a flow rate of 100 mL/min at 450 °C for 1 h. The obtained samples were rinsed using double distilled water through soxhlet extractor at 100 °C and oven dried. The prepared samples were sieved to obtain the desired particle size of 170–400 mesh size (Al-Othman et al., 2012). In the case of matured tea leaves, it was initially subjected for boiling numerous times in distilled water until the supernatant was clear. The cleaned biomass was oven dried, grounded and finally sieved. The biomass was then impregnated with phosphoric acid and placed in hot air oven at 100 °C for the time duration of 3 h. Thermal treatment of the impregnated biomass conducted in tube furnace, by heating up to 500 °C with the holding time of 1 h under the nitrogen flow. The obtained carbon material was washed using 0.1 M HCl (Mridusmita et al., 2014). Jinbei et al. (2015) carbonized 100 mesh size sieved longan seed and subsequently treated with sodium hydroxide. The prepared carbonized mixture activated in N_2 atmosphere at temperature of 600–800 °C with time duration of 0.5 - 1.5 h. The resulted activated carbon was washed with distilled water, hot air oven dried and sieved to obtain 100 mesh screen size adsorbent (Jinbei et al., 2015). After washing the Ficus carica fiber with deionized water for several times, extraction process performed in soxhlet using acetone and the obtained sample was vacuum oven dried. The sample sized to 1 mm and carbonized in muffle furnace at 700 °C for 5 min. About 25 g of the carbonized sample was mixed with 70 mL of phosphoric acid and activation was carried out in a microwave oven with input power of 600 W and irradiation time of 5 min. The obtained activated carbon was washed and oven dried (Vinod et al. 2013b).

5. CONCLUSIONS

The toxic heavy metal hexavalent chromium, regarded as one of a major heavy metal pollutant from industrial effluent, acts as the serious threat to the living system and natural environment. Biosorption is an effective process for the removal of hexavalent chromium from industrial wastewaters. Various lignocellulosic biomasses have been reported in the unmodified or modified form for the removal of hexavalent chromium from aqueous solutions. This review briefly summarizes the biosorption process using lignocellulosic sources, preparation of raw as well as modified form of biosorbents and presents the data of adsorption capacity towards hexavalent chromium removal. The summarized procedures of lignocellulosic biomass preparation and the data of adsorption capacity may be useful for the preparation of novel biosorbents and its application for the removal of hexavalent chromium from industrial effluent. Lignocellulosic materials being the waste biomass may be used as adsorbents and can be employed as substitute to the available commercial activated carbons. Most of the biosorption studies for hexavalent chromium removal using lignocellulosic biomass reported in batch level only, additional research is thus necessary in the directions of pilot and industrial scale.

ACKNOWLEDGEMENTS

The authors acknowledge the Science and Engineering Research Board, Department of Science and Technology, India for the award of post-doctoral research grant (PDF/2016/000284). The authors thank the department of Biotechnology and Medical Engineering, National Institute of Technology Rourkela for the research facility.

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