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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 ecofriendly 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