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A SURVEY OF MODIFIED AGRICULTURAL WASTES FOR HEAVY METAL REMOVAL FROM WASTEWATER

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ABSTRACT

Heavy metal removal from wastewater is of special concern due to presence of heavy metals in environment. The discharge of various industries contains heavy metals and they affect soil fertility, water resources, aquatic organisms and ecosystem integrity. The heavy metals which mainly discharge from industries are cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), nickel (Ni), selenium (Se), vanadium (V), cobalt (Co), mercury (Hg), lead (Pb), zinc (Zn) and arsenic (As). Among various processes, adsorption process is relatively new process for removal of heavy metals from wastewater. Adsorption has certain advantages over conventional methods such as they minimize chemical and biological sludge, possess low cost, high efficiency, possibility of metal recovery and adsorbent regeneration. Thus, this review article aims to compile scattered available information on modified agricultural adsorbent for heavy metal removal.

KEYWORDS: Adsorption; Agricultural waste; Heavy metal; Wastewater

INTRODUCTION

The discharge of toxic effluents from various industries affects soil fertility, aquatic organisms and water resources. These heavy metals can cause physical discomfort and life threatening illness. Industrial waste water contains polluting substances such as inorganic, organic, elemental and polymeric products (Kumar & Bandyopadhyay., 2006). The major heavy metal comes out from industries which are hazardous are nickel (Ni), iron (Fe), cadmium (Cd) and chromium (Cr), zinc (Zn), lead (Pb) and mercury (Hg). In India, the current maximum contaminant level (ppm – mg/L) for heavy metals is 0.20, 0.1, 0.01, 0.05, 0.80, 0.006, 0.00003 for nickel (Ni), iron (Fe), cadmium (Cd), chromium (Cr), zinc (Zn), lead (Pb) and mercury (Hg) respectively (Feng et al., 2009). Nickel can cause lung cancer, asthma, allergic reactions and heart disorders, Iron can cause conjunctivitis, choroiditis and retinitis if it contacts and remains in the tissue, cadmium (Cd) accumulate in human body, bones and kidney and it cause cancer. Past disaster due to contamination of cadmium in wastewater are " itai itai " in Jintsu river of Japan (Friberg and Elinder,1985; Kjellstrom et al., 1977). Chromium exists in two oxidation forms trivalent and Hexavalent form. Hexavalent chromium is more harmful than trivalent chromium. Zinc is essential for human health but large quantities of zinc can cause skin irritation, stomach cramps, vomiting and anaemia (Oyaro et al., 2007). Similarly, lead is harmful to human health and can damage to kidney, liver, reproductive system and brain functions (Naseem & Tahir 2001). Mercury is also harmful and it is a neurotoxin that can affect the central nervous system. If it is exceeded in concentration it can cause pulmonary, chest pain and dyspnoea (Namasivayam & Kadirvelu 1999). Conventional treatment technology for removal of heavy metals are chemical precipitation, ion exchange, chemical oxidation / reduction, reverse osmosis , electrodialysis, ultrafiltration but they are not economical (Fu & Wang, 2011). However, Adsorption is a powerful method for heavy metal sequestration from wastwater because they have low cost, minimization of sludge, adsorbent regeneration and possibility of metal recovery. Some low cost adsorbents used are hazelnut shell, orange peel, maize cobs, peanut shell, soyabean hulls, water hyacinth pulp powder, rice husk, brown sea weed, jack fruit, coconut fibre pith, coconut shell fibre, plant bark, pine needle, cactus leave, neem leave powder, rice brine, wheat brine, saw dust, cob and jathropha oil cake. These

agricultural waste materials are used either in a natural form or after some physical or chemical modifications to increase their removal capacity.

MATERIALS AND METHODS

Mechanism of biosorption

The removal of heavy metals from wastewater using agricultural material is due to biosorption (Volesky and Holan, 1995). Biosorption is a physiochemical process which occurs naturally in certain biomass which allows it to concentrate and bind contaminants onto its cellular structure. Biosorption process has a sorbent and solvent and this solvent consists of species which we have to be adsorbed on sorbent. These sorbents have affinity for metal ions species. These metal ions are attracted by sorbent and bound by complex process. Agricultural waste materials consist of cellulose and lignin and other components are hemicellulose, lipid, protein, water, starch, ash etc and many more compounds. Cellulose is an organic compound, a polysaccharides consisting of linear chain of several hundred to many thousand of β linked D-glucose units (Demirbas, 2000). However, Lignin is a complex polymer of aromatic alcohols known as monolignols. It is most commonly derived from wood and it is an integral part of the secondary cell walls of plants and some algae. These compounds contains functional groups such as, carbonyl, amido, amino, phenolic, carboxyl group, alchohols, ester and sulphydryl (Gupta & Ali, 2000). These groups have capability of complex formation.

Modified agricultural wastes

Agricultural wastes has recently gained attention in the field of heavy metal removal from wastewater because of their abundance and renewable nature. Agricultural wastes are further modified to increase their adsorption capacity. Pretreatment of agricultural wastes can extract soluble organic compounds and enhance chelating efficiency (Gaballah et al., 1997). Pretreatment methods was performed by using different kinds of modifying agents such as base solutions (sodium hydroxide, sodium carbonate calcium hydroxide), mineral and organic acid solutions (hydrochloric acid, nitric acid, sulfuric acid, tartaric acid, citric acid, thioglycollic acid), organic compounds (ethylenediamine, formaldehyde, epichlorohydrin, methanol) and oxidizing agent (hydrogen peroxide) for the purpose of increasing efficiency of metal adsorption (Hanafiah et al., 2006; Reddy & Parupudi., 1997; Taty-Costodes et al., 2003). Following modified agricultural wastes has been used for removal of heavy metal ions.

1. Modified rice husk

Rice husk consists of cellulose (32.24%), hemicellulose (21.34%), lignin (21.44%), mineral ash (15.05%) and silica (96.34%) (Rahman & Ismail, 1993). Rice husk is insoluble in water and it has good chemical stability, high mechanical strength, possesses a granular structure which makes it a good adsorbent material for treating heavy metals from wastewater. There are many chemicals which are used for modification of rice husk such as Hydrochloric acid (Kumar & Bandyopadhyay, 2006), sodium hydroxide (Guo et al., 2003; Kumar and Bandyopadhyay, 2006), sodium carbonate (Kumar and Bandyopadhyay, 2006), epichlorohydrin (Kumar and Bandyopadhyay, 2006) and tartaric acid (Wong et al., 2003). Kumar and Bandyopadhyay (2006) have used sodium hydroxide, sodium carbonate and epichlorohydrin for enhancing the adsorption capacity of cadmium. However, Tarley et al, 2004 has found that adsorption of Cd increases twice when rice husk was treated with NaOH. It was observed that the adsorption capacities of Cd were 7 and 4 mg/g for NaOH treated and unmodified rice husk, respectively.

2. Spent grain

Treatment of spent grain with NaOH enhances adsorption capacity for removal of Cd(II) and Pb(II) ions (Ngah & Hanafiah 2008). The reason behind increment in adsorption of heavy metal ions after base treatment is increase in the amount of galactouronic acid groups after hydrolysis of O-methyl ester groups. It was observed that the equilbrium time of adsorption was 120 min for both cadmium and lead metal ions and adsorption followed pseudo-second-order model. The maximum adsorption capacity for lead was two times higher than cadmium (Low et al., 2000).

3. Wheat bran

Wheat bran, a by-product of wheat milling industries and proved to be a good adsorbent for removal of heavy metal ions such as Pb(II), Cu(II) and Cd(II). O¨ zer et al., 2004 has used strong dehydrating agent like sulfuric acid (H_2SO_4) which eventually results in better efficiency of adsorption of copper. Then it was observed that maximum adsorption capacity for Cu(II) ions was reported as 51.5 mg/g (at pH 5) and equilibrium time of

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adsorption was achieved in 30 min. O¨ zer & Pirincci, 2006 has also treated wheat bran with sulfuric acid for cadmium ion removal from wastewater. After 4 hr of contact time, the maximum adsorption capacity that could be achieved for cadmium was 101 mg/g at pH 5. The order of maximum removal of the above three metals follows: Cd(II) > Pb(II) > Cu(II).

4. Saw dust

Sawdust is obtained from wood industry and it is an abundant by-product which is easily available. It has various organic compounds such as lignin, cellulose and hemicelluloses with polyphenolic groups (Ngah & Hanafiah 2008). These groups has capability to bind heavy metal ions. Kadirvelu et al., 2003 has used concentrated sulfuric acid for modification of coconut tree sawdust and removed mercury and nickel from wastewater. However, Shakirullah et al., 2006 has used sodium hydroxide for treatment of sawdust and removed nickel from wastewater. After treatment of sawdust with sodium hydroxide, methyl esters which are the major constituents in cellulose, hemicellulose and lignin has been converted into carboxylate ligands. The maximum adsorption capacity of Ni^{2+} ions was found to be 10.47 mg/g.

RESULTS AND DISCUSSION

A large number of agricultural wastes have been modified using various chemicals. It was also observed that after treatment with chemicals, the removal efficiency of adosrbents has been increased. Different agricultural wastes has been tabulated in Table.1 with their removal efficiency.

Table.1 Various modified agricultural wastes as an adsorbent for heavy metal removal

Adsorbent	Modifying agent	Heavy metal	Adsorption capacity (mg/g)	Optimum pH	References
Corn stalk	nitric acid	Cu	.325 mmol/g	4.5	Vafakhah et al., 2014
	diethylenetriamine	Cr	200	2-6	Chen et al.,2011
	phosphoric acid	Zn	79.21	-	Buasri et al., 2012
	corn cob silica with alginate	Cu Cd	4.73 4.60	> 3	Shim et al., 2014
Modified orange peel waste	methyl acrylate	Cu	289	2-6	Feng et al., 2009
	methyl acrylate	Pb Ni Cd	476.1 162.6 293.3	2-5.5	Feng et al., 2011
Rice husk	water washed	Cd	8.58	9	Kumar & Bandyopadhyay., 2006
	sodium hydroide		20.24		
	sodium bicarbonate		16.18		
	epichlorohydrin		11.12		
Walnut sawdust	formaldehyde in sulphuric acid	Cd Ni Pb	4.51 6.43 4.48	–	Bulut and Tez, 2003
Corncorb	nitric acid citric acid	Cd	19.3 55.2	3-6	Leyva-Ramos et al., 2005
Sugarcane bagasse	sodium bicarbonate ethylenediamine triethylenetetramine	Cu, Pb,Cd Cu,Pb,Cd Cu,Pb,Cd	114, 196, 189 139,164, 189 133,313, 313	5.8, 6.2, 7	Karnitz et al., 2007

CONCLUSION

This review article shows that the study on chemically modified agricultural plant for heavy metal removal has attracted the attention of many researchers. Mostly acid and bases were used for modification of agricultural wastes. After chemical modification the adsorption capacity of adsorbents has been increased due to increases in number of active binding sites, better ion-exchange properties and formation of new functional groups and it favours metal uptake. Although, after chemical modification adsorption capacity has been increased but cost of chemicals used and method of modification must have to be taken into consideration in order to produce 'low-cost' adsorbents

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