An Overview of Fruit Waste as Sustainable Adsorbent for heavy metal Removal

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Abstract. Biosorption is an environmental friendly method for metal removal as it can be used as a cost effective and efficient technique for heavy metal removal. A lot of biomass can be choosed as biosorbent such as waste material from food processing and agriculture.ent. This paper will review the potential used of local fruit rind as biosorbent for heavy metal removal in wastewater. Heavy metals have been in various industries and resulted to a toxic condition in aquatic ecosystem. Therefore, various techniques have been employed for the treatment of metal-bearing industrial wastewaters including biological treatment through biosorption. Biosorption offers the advantages of low cost, good efficiency and production of sludge with high metal content is possible to avoid by the existence of metal recovery method from metal loaded biosorbent. The successful application of local fruit waste in treating wastewater containing heavy metals requires a deeper understanding of how biosorbent material proceeds.

Introduction

Rapid industrialization and development released excessively heavy metals into the environment. Industries such as mining, metal plating and battery manufacturing, result in the release of heavy metals to aquatic ecoystem. Hence, it is important to remove heavy metal from the waste stream. [1].

Heavy metals are applied to a group of metals and metalloids with atomic density five times more than water. The most toxic form of these heavy metals in their ionic species. In the environment, the heavy metals are generally more persistent than organic contaminants such as pesticide or petroleum byproducts. The heavy metals can become mobile in water and soil depending on water and soil specification [2]. Heavy metals are non-biodegardable, entry into the food chain can result in accumulation through the food chain and biomagnifications[3], which increases the toxicity, thus increasing its threat to the ecosystem and human health[4]. Therefore, removal of heavy metal is one of the most important environmental issues worldwidely.

In Malaysia, the generation of waste containing heavy metals originates from electroplating and metal treatment or fabrication industries located along the West coast of peninsular including Klang Valley, Penang, Ipoh and Johor Bahru. Table 1 summarizes the heavy metals commonly released by industries and their sources. Table 2 summarizes permissible limit to Malaysia and International bodies on metal discharge.

The discharge of the effluents into the receiving environment should follow acceptable level and is a chief concern Various techniques have been employed for the treatment of metal-bearing industrial wastewaters. Conventional procedures include chemical precipitation [5], lime coagulation [6], ion exchange [7], reverse osmosis [8] and solvent extraction. These methods have been found to be limited since they often resulting problems of safely storing radioactive wastes [9], high capital and operational cost [10] and not economically feasible [11].

Table 1: Types of heavy metals and their effect on human health

Table 2: Heavy metals permissible limits for metal discharge

Metal	Permissible limit for industrial effluent discharge (mg/l)		Permissible limit by International bodies (mg/l)	
	Standard A	Standard B	WHO	USEPA
Lead	0.10	0.5	0.01	0.005
Cadmium	0.01	0.02	0.003	0.005
Mercury	0.005	0.05	0.001	0.002
Nickel	0.2	1.0	5.0	0.1
Arsenic	0.05	0.10	0.01	0.05
Copper	0.20	1.0	-	1.30

The need for more economical and effective method for metal removal from wastewater, have initiated all researchers world widely to search for efficient eco-friendly and cost-effective remedies. Hence, this search has directed to the discovery of biosorption. Biosorption is a technique that employs inactive non-growing biomass for the recovery of heavy metals from aqueous solutions. Biosorption offers the advantages of low cost, good efficiency and production of sludge with high metal content is possible to avoid by the existence of metal recovery method from metal loaded biosorbent through elution or incineration treatment [12]. Therefore, a low cost sorbent with high metal binding need to be investigated. The question arises, which waste as a good sorbent. Therefore, more studies should investigate waste material containing large amount of polysaccharides with acidic functional group namely, fruit waste.

Biosorption mechanisms by fruit biosorbents

The biosorption process using fruit biosorbent involves a solid phase (fruit waste, biomass or biosorbent) and a liquid phase (solvent, normally water) containing dissolved species to be sorbed (sorbate or metal). Due to the higher affinity of the biosorbent for the sorbate, the latter is attracted and bound there by different mechanisms. This process is continuous until the amount of solid-bound sorbate species and its portion remaining in the solution reach equilibrium Biosorption mechanisms can be varied due to the complex structure of biomass such as fruit waste which implies that there are many ways for the metal to be taken up by the cell. The status of biomass (viable or non-viable cell), property of metal solution chemistry, environmental conditions such as pH and temperature, influence the mechanism of metal biosorption. [13]. The mechanisms of biosorption are generally based on physico-chemical interactions between metal ions and the functional groups present on the cell surface, such as complexation, physical adsorption, ion exchange, chemical sorption, co-ordination and precipitation [14][15]. In complexation, the metal removal from solution may also take place by complex formation on the cell surface after interaction between the metal and the active groups. For ion exchange, the cell wall of the fruit waste that contains polysaccharides and bivalent metal ions exchange with the counter ions of the polysaccharides. The biosorption of Pb(II), Cd(II) and Co(II) by *Garcinia mangostana* L.fruit shell was expected to taken up by ion exchange mechanism [16]. In the category of physical adsorption, it takes place with the help of Van der Waal's forces. In the case of precipitation, it might be dependent or independent of cellular metabolism. The precipitates may be formed and remain in contact with or inside the microbial cells or independent of the solid phase of the cells. Purified products from isolated cells such as chitin accumulate greater quantities of cations than the intact cells providing that biomolecules can form metal precipitates.

Factors affecting biosorption

Biosorption is mainly affected by initial metal ion concentration, temperature, pH and biomass concentration in solution. Higher initial metal ion concentration results in a high solute uptake. This is because at higher concentration, the sites available for sorption become fewer compared to the moles of solute present, hence, the removal of solute is strongly depend upon the initial solute concentration. It is necessary to identify the maximum saturation potential of a biosorbent because all experiments for biosorption should be conducted at the highest possible initial solute concentration.

Temperature does not influence the efficiency of biosorption in the range of 20-35° C [17]. Higher temperature enhances sorption due to the increased surface activity and kinetic energy of the solute. However, physical damage to the biosorbent can be expected at higher temperature.

pH is observed to be very important due to its ability to affect the solution chemistry of the metals, the activity of functional groups in the biomass and the competition of metallic ions [18] [19]. pH strongly influences the specification and biosorption availability of the metal ions. At higher solution pH, the solubility of metal complexes decreases sufficiently allowing precipitation, which may complicate the sorption process.

The specific uptake of metal is influenced by the concentration of biomass in the solution. [20]. Many studies indicated that, lower biosorbent dosages yield higher uptake and lower percentage removal efficiencies. An increase in the biomass concentration generally increases the amount of solute biosorbed, due to the increased surface area of the biosorbent, which in turn increases the number of binding sites.

Fruits as biosorbent

Fruits and it by-products have been widely investigated for their potential to remove metals from water. These include coconut shell [21], durian rind [22], banana peel [23], mango peel [24], mangosteen shell [16], pomegranate peel [1], mandarin peel [25], papaya wood [26], yellow passion-fruit shell [27], grape waste [28], orange peel [29], coconut coir [30] and citrus peels [31]. Fruit wastes are cheap, unlimited, easily disposed by incineration, and even reusable after being rejuvenated. A study have reported successful desorption and rejuvenation of metal-loaded papaya wood using 0.1 HCl. The rejuvenated papaya wood retained its efficiency to biosorb copper and cadmium after five repeated cycles of sorption-desorption. Optimum biosorption for all three metals was reached at pH 5 during contact time of 60 minutes with relative order of metal sorption affinity of Cu (II) > Cd (II) > Zn (II) [32]. Sorption of Cr (III) and Pb (II) from aqueous solution by yellow passion fruit shell (YPFS) was studied by Jacques et. al [27]. The study presented that YPFS have higher adsorption capacities when compared with several different adsorbent of 151.6 mg^{-1} and 85.1 mg^{-1} respectively for Pb (II) and Cr (III). Removal of Cr (VI) from aqueous solution by crossed-linked grape waste gel was reported by Chand et. al [28]. Effect of process parameters (pH and contact time) was studied and sorption was most efficient at pH 1 during contact time of 60 minutes. The metal adsorption on the gel was highly pH dependent and the adsorption capacity was found to increase with increasing solute concentration. Adsorption behavior of Cd^{2+} and Pb^{2+} on mango peel waste (MPW) was studied by Iqbal et. al [24]. The adsorption of the metals was dependent on such experimental conditions like pH, sorbate-sorbent concentrations and contact time. Maximum adsorption for both Cd^{2+} and Pb^{2+} by MPW was reported at pH 5. The result showed 99% of both metals were removed in 60 minutes contact time. Experimental and reaction kinetics were expressed by Langmuir adsorption isotherm and pseudo-second order kinetics model. The potential to remove Pb^{2+} from aqueous solution by honey dew waste was reported by Akar et. al. [33]. The biosorption was rapid in the initial stage of the process and increased with an increase in contact time up to 80 minutes at pH 5.5. The temperature positively affecting the biosorption efficiency of biosorbent for metal ion where the biosorption capacity increased from 52.09 ± 1.47 mg^{-1} to 75.88 ± 0.75 mg^{-1} where the temperature was raised from 20° C to 40° C. Table 3 presents a comparison of several fruit biosorbents.

Table 3:Comparison of several fruit biosorbents.

Biosorbent	Target Heavy metal	Parameter
Coconut coir	Pb	pH-2 ; Time-10min; Uptake-26.5mg/g
Mangosteen shell	Pb	pH- 2-5; Time-30min; Uptake-3.6mg/g
	Cd	pH- 4; Time-30min; Uptake-3.15mg/g
Yellow passion fruit shell	Pb	pH- 5; Time-120min; Uptake-151.6mg/g
Grape waste	Cr	pH- 4; Time-60min; Uptake-1.91mg/g
Papaya wood	Cd	pH- 5; Time-60min; Uptake-19.88mg/g
	Cu	pH- 5; Time-60min; Uptake-19.89mg/g
Mango peel	Pb	pH- 5; Time-60min; Uptake-99.05mg/g
	Cd	pH- 5; Time-60min; Uptake-68.92mg/g

The table shows that various type of fruit biosorbent had been used to different kind of target heavy metals. Each fruit biosorbent need different condition of pH, contact time and yield different metal uptake. The results also show that fruits are a promising biosorbent. As stated in the earliest discussion the cell wall of fruit waste containing polysaccharides help to absorb target heavy metals.

In Malaysia, diverse industries discharge effluent containing a mixture of pollutant including heavy metals. Therefore, there is a great potential of using other locally fruit waste material as biosorbent in treating the wastewater containing heavy metals. Fruit waste materials are typically generated large quantities by the fruit juice industry or fruit stall locally. These materials have received little scientific attention, in spite of high quantity of pectin, which contain carboxyl group. The plant cell wall polysaccharide pectin consists mostly of polygalacturonic acid (carboxyl group). Normally, polysaccharide pectin is commercially extracted from sugar beat, apple and citrus peels. Due to similarity of pectin, such fruit materials namely banana, watermelon or honeydew are predicted as a very promising biosorbent. However their biosorption potential has only been studied to a limited extent in spite of their abundant availability at minimal cost.

This alternative sorbent material is choosed based on its potentially high content of cellulose, pectin, hemicellulose and lignin and due to its abundance as waste material from juice industry or fruit stall. Beside the fact the fruit is rich in nutrition, the rind contain high pectin which is essential component for sorbent material as active sites. The active binding sites for metals are supposed functional group of hydroxyl and carboxyl in cellulose, chemical modification has shown great promise in improving the cation exchange capacity due to the increase of functional group. In the previous work, adsorption of metal were studied by using raw citrus peel and resulted to different affinity sequence [25].

Concluding remark

Taking into account that biosorption technology has proven to be effective, economic and environmental friendly for the treatment of wastewater containing heavy metals, focused research in a more comprehensive area is desired for more effective treatment design and performance. Some areas where further research may be directed include strategies to enhance performance of biosorbent and mass transfer of contaminant, optimization of process factors, system congfiguration and multiple process integration. This review has highlighted that biosorbent is a potential method in treating heavy metal in wastewater.

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REFERENCES

[1] E.-S.Z. El-Ashtoukhy., N.K. Amin. and O.Abdelwahab. (2008). Removal of lead (II) and copper (II) from aqueous solution using pomegranate peel as new adsorbent. Desalination. 223, 162-173.

[2] T.V , Ramachandra., N. Ahalya., and R.D Kanamadi. (2008). Biosorption :Techniques and Mechanisms. CES Technical Report 110.

[3] K. Vijayaraghavan. and Y-S Yun. (2008). Bacterial biosorbents and biosorption. Biotechnology Advances. 26, 266–291.

[4] H. K. Alluri., S. R. Ronda., S.S Vijaya., S.B Bondili., V. Suryanarayana. and P. Venkateshwar. (2007). Biosorption: An eco-friendly alternative for heavy metal removal. African Journal of Biotechnology Vol. 6 (25), 2924-2931.

[5] A. Ozer., H.S.Altundogan., M. Erdem and F ,Tunmen. (1997). A study on the Cr(VI) removal from aqueous solutions by steel wool. Environmental Polution. 97, 107-112.

[6] G.M Ayoub., A. Hamzeh, L. and Semerjian. (2011). Post treatment of tannery wastewater using lime or bittern coagulation and activated carbon adsorption. Desalination. 273, 359-365.

[7] S. Rengaraj., C. K. Joo., K. Younghun. and Y. Jongheop. (2003). Kinetics of removal of chromium from water and electronic process wastewater by ion exchange resins: 1200H, 1500H and IRN97H. Journal of Hazardous Materials. B102, 257–275.

[8] M. Mohsen-Nia., P. Montazeri. and H. Modarress. (2007). Removal of Cu^{2+} and Ni^{2+} from wastewater with chelating agent and reverse osmosis. Desalination.143, 276-281.

[9] Z.G. Guiragossian., G.A. Martoyan., S.G. Injeyan., S.G. Tonikyan. and G.G. Nalbandyan. (2003). The extraction of heavy metals by means of a new electrolytic method. W.M'03 Conference, Tucson AZ.

[10] G. H.Pino., L. M. Souzo de Mesquita., M. L. Torem. and G. A. S. Pinto. (2006). Biosorption of cadmium by green coconut shell powder. Minerals Engineering. 19, 380-287.

[11] H. Michael. and I. Ayebaemi. (2005). Effect of metal ion concentration on the biosorption of Pb^{2+} and Cd^{2+} by Caladium bicolour (wild cocoyam). African Journal of Biotechology. 4, 191-196.

[12] B. Volesky (1990). Biosorption of Heavy Metals. CRC Press, Boca Raton, USA, 396.

[13] B Volesky. and Z. R. Holant. (1995). Biosorption of Heavy Metals. Biotechnol Prog. 11, 235-250.

[14] M. Tsezos., E. Remoundaki. and A. Hatzikioseyian. Biosorption - principles and applications for metal immobilization from waste-water streams. National Technical University of Athens (NTUA).

[15] N. Ahalya., T.V. Ramachandra. and R.D. Kanamadi. (2003). Biosorption of Heavy Metals. Research Journal Of Chemistry And Environment. Vol 7(4).

[16] R. Zein., R. Suhaili., F. Earnestly., Indrawati. and E. Munaf. (2010). Removal of Pb(II), Cd(II) and Co(II) from aqueous solution using Garcinia mangostana L. fruit shell. Journal of Hazardous Materials. 181, 52-56.

[17] Z. Sag Y. and T. Kutsal. (1992). The biosorption of copper by C. vulgaris and Z. ramigera. Environmental Technology. 13, 579-586.

[18] M. Friis. and M. Keith. (1998). Biosorption of uranium and lead by Streptomyces longwoodensis. Biotechology Engineering. 35, 320-325.

[19] M. Galun., E. Galun., B.Z, Siegel., P. Keller. and H. Lehr. (1987). Removal of metal ions from aqueous solutions by Penicillum biomass: Kinetic and uptake parameters, Water, Air, Soil Pollution. 33, 359-371.

[20] E. Fourest. and J.C. Roux(1992). Heavy metal biosorption by fungal mycellial by-products : Mechanism and influence of Ph. Applied Microbial Biotechnology. 37, 399-403.

[21] G. H.Pino., L. M. Souzo de Mesquita., M. L. Torem. and G. A. S. Pinto. (2006). Biosorption of cadmium by green coconut shell powder. Minerals Engineering. 19, 380-387.

[22] W. W. Wong., F.M.A., Liong. and Azhar M.E. (2008). Technical-short communication Modification of Durian rind pectin for improved biosorbent ability. International Food Research, 15.

[23] P. Kaewsarn., W. Saikaew. and S. Wongcharee. (2008). Dried biosorbent derived from Banana peel : A potential biosorbent for removal of cadmium ions from aqueous solution. Presented at The 18h Thailand Chemical Engineering and Applied Chemistry Conference October 20-21,2008,Pattaya Thailand.

[24] M. Iqbal., A. Saeed. and S. I. Zafar. (2009). FTIR spectrophotometry, kinetics and adsorption isotherms modelling, ion exchange and EDX analysis for understanding the mechanism of Cd^{2+} and Pb^{2+} removal by mango peel waste. Journal of Hazardous Materials. 164, 161-171.

[25] F. A. Pavan., I. S. Lima., E.C.Lima., C. A. and Y. Gushikem. (2006). Use of Ponkan mandarin peels as biosorbent for toxic metals uptake from aqueous solutions. Journal of Hazardous Materials. 137, 527-533

[26] M. Asma Saeed, W. Akhter. and M. Iqbal. (2005). Removal and recovery of heavy metals from aqueous solution using papaya wood as a new biosorbent. Separation and Purification Technology. 45, 25-31.

[27] Rosangela A. Jacques, Eder C. Lima., Silvio L.P. Dias., Ana C. Mazzocato. and Flavio A. Pavon. (2007). Yellow passion-fruit shell as biosorbent to remove Cr(III) and Pb(II) from aqueous solution. Separation and Purification Technology. 57. 193-198.

[28] R. Chand., K. Narimura., H. Kawakita., K. Ohto., Takanori Watari. and Katsutoshi Inoue. (2009). Grape waste as a biosorbent for removing Cr (VI) from aqueous solution. Journal of Hazardous Material. 163, 245-250.

[29] N. Feng., X. Guo., S. Liang., Y. Zhu. and J. Liu. (2011). Biosorption of heavy metals from aqueous solutions by chemically modified orange peel. Journal of Hazardous Material. 185, 49-54.

[30] H.G. Mario., C.L. Georgia., B. Claudia. E.A. Pelizaro.,. Menezes., G.L. Sherlan., G. B Sousa. and A. Rita A. Nogueira. (2008). Coconut coir as biosorbent for Cr (VI) removal from laboratory wastewater. Journal of Hazardous Material. 159, 252-256.

[31] E. Njikam. and S. Schiewer. (2012). Optimization and kinetic mpdeling of cadmium desorption from citrus peels. A process for biosorbent regeneration. Journal of Hazardous Material. 213-214, 242-248.

[32] N.Das., R. Vimala. and P. Karthika. (2008). Biosorption of heavy metals. An overview. Indian Journal of Biotechnology. 7, 159-169.

[33] S. T.i Akar., S.Arslan., T. Alp., D. Arslan. and T. Akar. (2012). Biosorption potential of the waste biomaterial obtained from Cucumis melo for the removal of Pb^{2+} ions from aqueous media : Equilibrium, kinetics, thermodynamic and mechanism analysis. Chemical Engineering Journal. 185-186. 82-90.