International Food Research Journal 15(3): 363-365 (2008)

Modification of durian rind pectin for improved biosorbent ability

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Abstract: Pectin and modified pectin differ in the structure of the chains in which the modified version of pectin is shorter in length, non-branched, and galactose-rich. These differences in structure may be exploited for the removal of heavy metals. Durian (*Durio zibethinus*) rind, that is regarded as agri-food waste was processed into durian rind pectin (DRP) and modified durian rind pectin (mDRP). DRP and mDRP were evaluated as biosorbent for removal of toxic heavy metals (Pb(II), Cd(II), Cu(II), Zn(II) and Ni(II)) and were compared with two commercial products; citrus pectin (CP) and modified citrus pectin (MCP). In general, the order of removal of heavy metals by all biosorbents was Cu(II) > Pb(II) > Ni(II) > Zn > Cd(II). Except for the removal of Pb(II), the order of effectiveness of heavy metal removal of the biosorbents was MCP > mDRP > CP > DRP. MCP, a commercial biosorbent showed the best biosorbent ability, and mDRP a waste product from durian was also a favorable sorber that should be considered for sorption and removal of heavy metals.

Keywords: Biosorbents, heavy metals, durian rind, durian rind pectin, modified durian rind pectin

INTRODUCTION

Heavy metals are dangerous because they tend to undergo a process of bioaccumulation. Their potential toxic effects accumulate within sensitive organs and tissues. In humans, poisoning by most of these metals causes severe dysfunction in the kidneys, reproductive system, liver, brain and central nervous system (Manahan, 1994).

Pectin are the ionic plant polysaccharides, whose main structural features are the linear chains containing more than 100 (1-4)-linked α-D-galacturonic acid residue (Schols and Voragen, 1996). Heavy metal binding ability of pectin has been reported by Kartel *et al.* (1999) and Khotimchenko *et al.* (2007). Modified citrus pectin (MCP) is a complex polysaccharide obtained from the peel and pulp of citrus fruits (mostly oranges). It is produced from citrus pectin via pH and temperature modification that breaks it into shorter, non-branched, galactose-rich carbohydrate chains. These shorter chains dissolve more readily in water and are better absorbed and utilized by the body than the long-chain pectin. Heavy metal removal ability of MCP in the blood stream of humans has been demonstrated by Eliaz and Rode (2003). Other than the heavy metal removal ability, MCP also has a binding affinity for galectins on the surface of cancer cells, resulting in an inhibition, or blocking of cancer cell aggregation, adhesion and metastasis (Raz and Loton, 1987). It can be envisaged that a conversion of conventional pectin into its modified counterparts has a huge potential for greater return on investment.

Durian (*Durio zibethinus*) is one of the famous fruit commodities in Malaysia and some other South East Asian countries. During the durian season the amounts of rind disposed as waste could lead to environmental problems. Water soluble polysaccharides that can be extracted from durian rind contain a high amount of pectin that could be further utilized for industrial uses (Hokputsa *et al.*, 2004). At pH 3 and in the presence of 65% sugar, durian rind pectin form strong gels suggesting the suitability of the product as a gelling agent (Easa, 2005). However the use of DRP or mDRP as a nutraceutical biosorbent has never been evaluated. Such an evaluation is expected to enhance the value of pectin from durian rind waste.

It is therefore important to improve on the value of this waste by performing chemical modification on durian rind pectin (DRP). The objective of this study was to explore the feasibility of using modified durian rind pectin (mDRP) for the removal of toxic heavy metals. mDRP may be further evaluated as a nutraceutical product.

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MATERIALS AND METHODS

Materials

Durian rinds were obtained from local fruits stalls in Penang, Malaysia. Citrus pectin (CP) was purchased from Sigma; Modified Citrus Pectin, MCP (PectaSol®) was obtained from EcoNugenics®; Metal cations were used as their salts; $Pb(NO_3)_2$, $NiCl_2$, $CuSO_4$ were purchased from Sigma; $ZnSO_4$ from Riedel-de-Haën, $CdCl_2$ from Fluka. All other chemicals used were of analytical grade.

Preparation of pectin from durian rind

The extraction method was modified from the combination methods described by McCready (1970) and Hokputsa *et al.* (2004). The durian rind (solid-liquid ratio; 1:9, w/v) were gently stirred in a mild acid aqueous solution adjusted to pH 2 with 1 M HCl. Then, the solution was extracted at 90°C for 4 hr. The resulting slurries were filtered through cheese cloth and allowed to cool to room temperature (25°C). Acidified ethanol (4% HCl in 95% EtOH) was added in the ratio 1:4 (v/v) and kept for 1 hr. The mixture was centrifuged at 3,000 rpm for 15 min in a Bench Top Centrifuge (Kubota 5100, Fujioka, Japan).

The gel-like precipitate was collected and re-suspended in distilled water in a ratio of 1:4 (w/v). Then, the solution was rewashed twice with 95% ethanol (1:2 v/v) and centrifuged for 15 min (3000 rpm). The precipitate was collected and dried in a vacuum oven at 25°C for 8 hr. The pectin was ground and sieved (mesh no.60) for further experiments. This pectin was designated as durian rind pectin or DRP.

Modification of durian rind pectin

The pH and temperature modification of DRP was performed according to Platt and Raz (1992) and Nangia-Makker *et al.* (2002). Initially, DRP was solubilized as a 1.5% solution in distilled water, and its pH was increased to 10.0 with NaOH (3N), followed by a 1 hr incubation at 50-60°C. Then, it was cooled to room temperature, the pH was adjusted to 3.0 with 3 N HCl and stored overnight. The samples were then precipitated the next day with 95% ethanol and incubated at -20°C for 2 hr, filtered, washed with acetone, and dried in a vacuum oven at 25°C for 8 hr. The pectin was ground and sieved (mesh no.60) for further experiments. This pectin was designated as modified durian rind pectin or mDRP.

Heavy metal biosorption

Adsorption studies were performed according to Kartel *et al.* (1999) and Senthilkumaar *et al.* (2000) with slight modification. One percent (w/v) of different pectins was added into 100 ml flasks containing 50 ml of a 10 mMol/l solution of metal salts. The flasks were agitated under constant stirring for 2 hr at room temperature. The liquid and solid phases were separated by centrifugation at 3000 rpm for 5 min. The heavy metals in the supernatant were estimated using atomic absorption spectroscopy (Perkin Elmer Analyst 100). The experiments were carried out in triplicate and the results are presented as mean values ± standard deviation.

RESULTS AND DISCUSSION

The percent removals of heavy metals for different pectins are listed in Table 1. With the exception of Pb(II) removal, the order of effectiveness of heavy metal removal of the biosorbents was MCP > mDRP > CP > DRP. CP and MCP are commercial products that have been optimized and properly processed, which explains their ability to remove heavy metals. The removal of all heavy metals by mDRP was significantly ($P < 0.05$) higher than that of DRP. This suggests that the process of modification of DRP increased the binding of metal ions with carboxyl residues of pectin. Modified pectin that contains a low degree of esterification presumably exerts considerably higher sorption activity (Manunza *et al.*, 1998). This confirms the suggestion that chemical modification of pectin could enhance the adsorption capacity of heavy metals. The order

Table 1: Percent removal* of heavy metal ions by different pectins

Pectin types	Metal ions				
	Cd(II)	Cu(II)	Zn(II)	Pb(II)	Ni(II)
CP	38.43±2.75[b]	80.01±1.96[b]	41.56±2.31[b]	67.06±1.53[b]	52.43±2.86[b]
MCP	93.96±0.47[a]	98.40±0.16[a]	94.41±0.99[a]	97.89±0.16[a]	92.72±0.32[a]
DRP	10.52±0.69[c]	54.94±4.66[c]	8.46±0.83[c]	38.57±1.00[d]	26.12±2.54[d]
mDRP	40.04±1.61[b]	81.24±0.41[b]	42.50±2.11[b]	57.86±0.83[c]	53.58±0.53[c]

*Values are means ± SD of 3 measurements. Values in a column with different superscript letters are significantly different ($P < 0.05$)

of removal of heavy metals by mDRP was Cu(II) > Pb(II) > Zn(II) > Ni(II) > Cd(II). Optimization studies are ongoing to further improve the removal of heavy metals by mDRP. This is important since the removal of heavy metals is dependent on several factors such as pH values (Senthilkumaar *et al.*, 2000; Khotimchenko *et al.*, 2007), modification parameters of pectin (Platt and Raz, 1992; Nangia-Makker *et al.*, 2002) and perhaps the concentration of biosorbents.

CONCLUSION

The preliminary results show that the modification of durian rind pectin yielded a modified product with improved biosorbent ability that could be used for removal of heavy metals. The modified product may be developed into a nutraceutical product similar to that of MCP.

ACKNOWLEDGEMENTS

A short term grant from USM (304/PTEKIND/636071) is gratefully acknowledged. The authors would like to acknowledge Phuah Eng Tong for his assistance with analysis using the Atomic Absorption Spectrophotometer.

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