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ISOLATION AND UTILIZATION OF CORN COBS HEMISELLULOSE AS CHELATING AGENT FOR LEAD IONS

(Pemencilan dan Penggunaan Hemiselulos Daripada Tongkol Jagung Sebagai Agen Pengkelat Untuk Ion Plumbum)

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Abstract

Corn cobs is an agricultural byproduct containing polysaccharide composed of cellulose, hemicellulose and lignin. Hemicellulose has a hydroxyl and carbonyl functional groups which can be used as chelating agent for metal ions. The purpose of this study was to isolate and evaluate corncobs hemicellulose as a chelating agent toward lead ion. Graphite furnace spectrofotometry at 283.3 nm was used to determine the residual lead ion in solution. The research's result showed that the highest yield of hemicellulose (12.04%) was obtained from delignication with 0,03M NaOH in 60% ethanol and 3% H_2O_2, hemicellulose isolation with 500 ml of 0.2 M NaOH, and precipitation with 1 : 4 ratio of 10% acetic acid in 95% ethanol. The 300 mg corn cobs hemicellulose has chelating effect for 40mg lead solution at (39.52 ± 0.1350) mg or 98.80%, that the corn cobs hemicellulose can be used as a chelating agent for lead.

Keywords: corn cobs, isolation, hemicellulose, Pb, chelating agent

Abstrak

Tongkol jagung adalah sisa pertanian yang mengandungi polisakarida yang terdiri daripada selulos, hemiselulos dan lignin. Hemiselulos mempunyai gugusan berfungsi karbonil dan hidroksil yang boleh digunakan sebagai agen pengkelat ion logam. Tujuan kajian ini ialah untuk mengasingkan dan menilai hemiselulos tongkol jagung sebagai agen pengkelat ion plumbum. Spektrofotometri dapur grafit digunakan bagi menentukan plumbum dalam larutan pada 283.3 nm. Hasil kajian menunjukkan hasil hemiselulos tertinggi (12.4%) diperolehi daripada nyahlignin dengan 0,03M NaOH dalam 60% ethanol dan 3% H_2O_2 dan pengasingan hemilulos dengan 500 ml 0.2 M NaOH,dan pemendekan dengan 1:4 nisbah 10% asid asetik dalam 95% ethanol. Sebanyak 300 mg hemiselulos tongkol jagung menyerap 39.52 ± 0.1350 mg (98.8%) daripada 40 mg Pb, ini menunjukkan hemiselulos tongkol jagung boleh digunakan sebagai agen pengkelat Pb.

Kata kunci: tongkol jagung, hemiselulos, Pb, agen pengkelat

Introduction

Hemicellulose is one of most abundant polymer after cellulose. However, its potential has yet to be completely recognized. Hemicellulose comprises a variety of monomers including xylosa, mannose, arabinose, glucose, glukoronic acid having hydroxyl (OH) group on each monomer [1]. In the qualitative chemical analysis of organic compounds, the OH group in both cyclical aliphatic will be able to bind metal ions to form complex salts. Hemicellulose applications in the pharmaceutical field could potentially be developed as a dietary supplement or as drug formulation excipients such as binders, disintergrator, thickeners and stabilizers. In addition, several important applications of hemicellulose have been done by making the derivatives which have pharmacological effects such as lowering cholesterol, and inhibitors of HIV [2,3,4].

Corn cobs contains hemicellulose approximately 12.5% and is the largest amount in comparison with other species [5]. Several reseaches have been performed on the separation of hemicellulose from different plant byproducts with

different methods of isolation. Isolation of hemicellulose by using alkali such as KOH or NaOH at various concentrations have been reported [2,3,5].

Lead is a toxic element because it tends to undergo a process of bioaccumulation and potential toxic amount 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 [6,7]. The aim of this study is to isolate hemicelluloses from corn cobs and to test its ability to absorb lead in solution.

Materials and Methods

Materials

Corn Cobs were obtained from local Corn in Medan, Indonesia. Pectin Technical grade (China), NaOH (E.Merck), 35% H_2O_2 (E.Merck), 96% ethanol (E.Merck), CH_3COOH (E.Merck), $Pb(NO3)_2$ (E.Merck), Lead ion 1000 ppb/ml (E.Merck), All other chemicals used were of analytical grade.

Isolation of hemisellulose from corn cobs

The extraction method was modified from the combination methods described by [2,3,5]. The corn cobs powder of 50 grams was added to 500 ml of 0.03 M NaOH in 70% ethanol and heated at 60°C and stirred for 2 hours to dissolve the lignin. The suspension was allowed to cool to room temperature and filtered through Whatman filter paper. The precipitate was added 500 ml of 0.2 M NaOH, and stirred for 8 hours at room temperature to dissolve hemicellulose, and then filtered. The filtrate was heated at a temperature of 65°C, and added 137 ml of 3% H_2O_2 in stages. Each addition of 1 ml 3% H_2O_2 to the filtrate and stirred constantly, stirring was performed until the entire 3% $H_2O_2$is used, stirring is continued until a clear solution. Solution of 10% acetic acid in 95% ethanol with a ratio of 1:4 (v / v) was added to the sample solution and left at room temperature for 6 hours until the precipitate formed. The suspension was centrifuged at a rate of 10,000 rpm for 15 minutes, and the filtrate was discarded, the precipitate was washed with 96% ethanol, and dried in vacuum dryer. The washed precipitate is hemicellulose.

Lead absorption

The absorption method was modified from the methods described by Wong et al. [8]. The hemicellulose and pectin respectively weighed 100 mg, 200 mg and 300 mg, Then each dissolved into erlenmeyer containing 25 ml solution 40 mg/ml of lead in 0.1 N nitric acid and the pH adjusted with acid pH performed at pH 2, the solution was stirred with a magnetic stirrer at room temperature for 2 hours. Then each was centrifuged at 10,000 rpm for 30 minutes. The supernatant was taken and diluted with 0.5 ml to 50 ml aquabidest then 0.25 ml of dilution was taken and diluted to 25 ml with aquabidest and lead levels were measured. The Lead in the supernatant were estimated using graphite furnace atomic absorption spectroscopy (Hitachi Analyst 100). The results are presented as mean values ± standard deviation.

Results and Discussion

Isolation of Hemicellulose

Modified isolation of corn cobs hemicellulose using 500ml of 0.03M NaOH in70% ethanol and precipitation using the solution of 10% acetic acid in 95% ethanol with a ratio of 1:4 (v/v) and corn cobs hemicellulose obtained with levels of 12.03% and in accordance with the results of Ricahana 2006 research that levels of 12:04% [5]. Chelating ability of corn cobs hemicellulose and pectin toward lead ion is shown in Table 1.

Table 1 shows that the administration of chelating agent to bind lead at pH 2, the higher the amount of chelating agent showed an increase chelating ability, but in hemicellulose from corn cobs the increase was not in proportional with the amount of hemicellulose, it is in accordance with the principle of adsorption that the adsorption process will end if there is equilibrium between the adsorbent, so the weight does not affect a significant absorbance with the increasing amount of hemicellulose for each treatment.

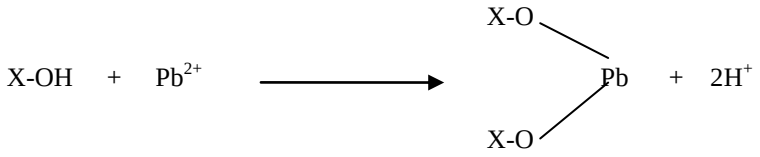
From Table 1 can be seen that there is the influence of the type of chelating agent and the weight of the chelating agent applied. Compare to hemicellulose, 100 mg pectin has the lowest binding capacity of 21.10 ± 1.08 mg of lead ion or 52.75%. But the 200 mg and 300 mg pectin will give a greater ability in binding capacity of 32.48 ±

0.71 mg or 81.20% and 37.39 ± 0.22 mg or 93.47% of lead ion respectively which show that the corn cob hemicellulose has greater chelating effect than pectin.

Table 1. Chelating effect of Corn Cobs Hemicellulose and Pectin for 40mg/25ml lead ions.

Chelating agent	Weight	Lead content in Chelating agent (mg)	Percentage lead ion in Chelating agent (%)
Hemicellulose	100 mg	35.97 ± 0.25	89.92
	200 mg	37.33 ± 1.90	93.32
	300 mg	39.53 ± 0.13	98.82
Pectin	100 mg	21.10 ± 1.08	52.75
	200 mg	32.48 ± 0.71	81.20
	300 mg	37.39 ± 0.22	93.47

Absorption characteristics between hemicelluloses and pectin are different where hemicelluloses reacts with lead ions. This suggests that the hydroxyl group of the hemicellulose causes attraction of lead ions present in solution, thus hemicellulose is more polar and has a better absorption capacity than the less polar substances. Uptake mechanism that occurs between the-hydroxyl function from hemicellulose monomer for example xylose group attached to the surface with the positively charged metal ion (cation) is an ion exchange mechanism as follows:



Metal ion in the form of lead ions, -OH groups are hydroxyl groups present on the C atom of the monomer compound in the hemicellulose and X is a matrix of hemicellulose place the-OH group attached. Interactions between the-OH group with the lead ion is also possible through the mechanism of formation of coordination complexes as atomic oxygen (O) with -OH group has a lone pair, while the lead ion has an empty orbitals. The free electron pair will occupy a empty orbital which is owned by a metal ion, thus forming a compound or complex ion [9]. Chemical bonding that occurs between the active groups in the molecules of organic substances can be explained as the behavior of Lewis acid-base interactions which produce complex on the surface of solids. In the system of binding of metal ion solution, for example the interaction is written in general form,

$$2[FH] + M^{z} \longrightarrow [F_2M^{(Z-2)}]^{+} + 2H^{+}$$

with FH is a functional group found in organic matter, and M is the ion of z valency. This means that the in-vitro hemicellulose which is an organic compound having a hydroxyl group can bind to metal of two valency in the dissolved state and acidic conditions.

Conclusion

The modified method for isolation of corn cobs hemicelluloses gave a yield of 12.03%. Corn cobs hemicelluloses have the ability to bind lead at pH2 and the capacity was influenced by the weight and the highest was shown by the 300mg corn cobs hemicelluloses with binding capacity at 39.52 ± 0.1350 mg to 40mg of lead solution, or 98.80%. Corn cobs Hemicelluloses can be used as a chelating agent for lead.

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