CHAPTER 4 RESULTS AND DISCUSSION

4.1 Characterization of corn cobs

4.1.1 Ion exchange capacity and mass loss of chemically modified corn cobs

To prepare modified corn cob, unmodified corn cob was immersed in 0.1 M NaOH solution at 50 °C for 30 minutes. After that, it was immersed at room temperature for various times. Reaction between hydroxyl groups in cellulose of corn cob and NaOH converted hydroxyl groups to oxy groups. However, the reaction also led to the loss of corn cob mass. Corn cob immersed in the NaOH solution for 2 h showed undetectable IEC even though it lost 54% of mass. Increase in the immersion time to 4, 6 and 10 h resulted in an average ion exchange capacities was 0.25±0.004 meq/g dry sorbent. The corresponding average mass loss percent was 56±1.6. It could be the result of the high hemicellulose content of corn cob that caused the loss of mass. It was reported that hemicellulose was hydrolyzed or removed in the process of NaOH treatment. [30]

From the above results, IEC of corn cobs treated with 0.1 M NaOH for 4 h was the highest. Longer treatment time did not provide an increase in IEC. However, immersion at 50 °C for 4 h resulted in a higher IEC, 0.30 meq/g dry sorbent, while mass loss slightly increased from 56.83% to 58.72%. Therefore, the treating temperature was maintained at 50 °C for 4 h for all chemical modification in this work.

4.1.2 The soluble of the corn cob in water

Table 4.1 Mass loss of corn cobs in water at 80 ° C for 20 min

Adsorbent	Moisture content (%)*	Mass loss (%)* after 1st immersion	Mass loss (%)* after 2nd immersion
Unmodified Corn cobs	9.42±0.4	34.87±1.5	3.50±0.5
Modified Corn cobs	10.64±0.4	1.93±0.3	undetectable

* Based on dry mass basis

As green tea was generally brewed at 80 °C, the loss of adsorbent mass after the immersion in water at 80 °C for 20 minutes was determined. The result shown in Table 4.1 suggests that unmodified corn cob lost 34.87 % of its mass, which was close to the percent water-soluble hemicellulose [30], after the first immersion. The less mass loss was observed after the second immersion. In contrast, modified corn cob lost most of hemicellulose during the NaOH treatment. The mass loss after the first immersion was only 1.93%.

4.2 Adsorption of green tea using corn cobs without tea bag

4.2.1 Influence of heat treatment on adsorption performance

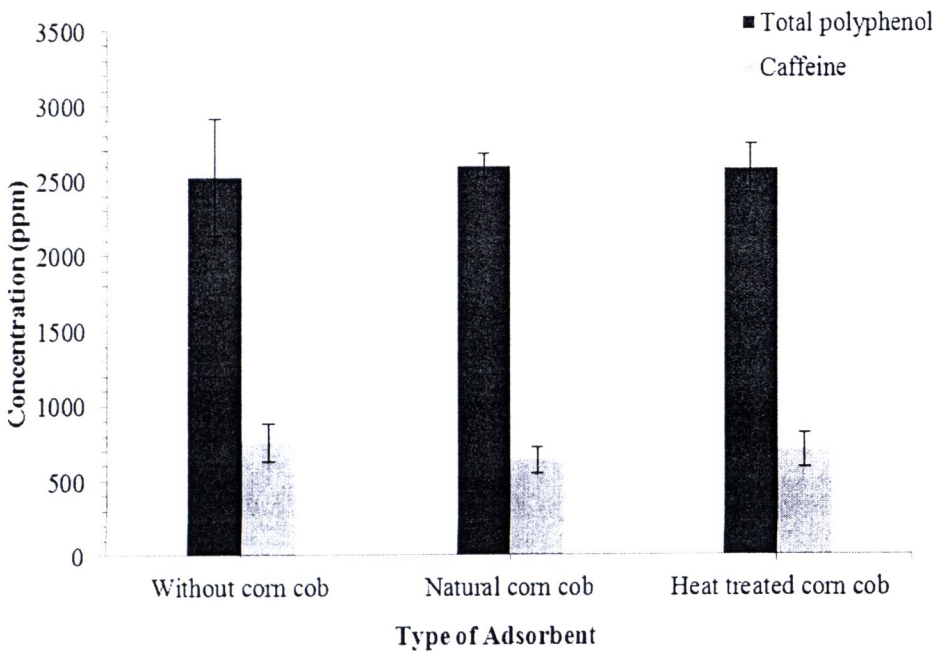


Figure 4.1 Caffeine and total polyphenol concentrations of adsorption using heat treated corn cobs as the adsorbent.

Within experimental errors, adsorbents could not adsorb caffeine and polyphenol as shown by Figure 4.2. The adsorption was carried out for 20 min using green tea solution at 80 °C. The heat treated corn cob was prepared by heating corn cob in 50°C water for 20 min. After the heat treatment, 30.37±2% of corn cob mass, part of which was water-soluble hemicellulose [30], was lost. If the natural and heat treated corn cobs had adsorbed caffeine and polyphenol, they would probably have used their hydroxyl groups. Because hydroxyl groups in lignocellulose had strong hydrogen bonding and did not interact with those of polyphenols, adsorption of polyphenol was not observed. Nonetheless, caffeine was slightly adsorbed by natural corn cob, while heat treated corn cob was unable to adsorb caffeine. The loss of hemicellulose likely was responsible for the lack of such inability.

4.2.2 Effect of functional groups on adsorption ability

The ability of corn cob in caffeine adsorption is discussed in this section. Unmodified and modified corn cobs, 1-1.4 mm. in size, were immersed in green tea solution at 80 °C for 1-20 minutes, while shaking at 150 rpm all the time. Figure 4.3 presents the decreased of caffeine content in green tea as a function of time.

Without any adsorbent, the caffeine concentration was approximately 757 ppm after 20 minutes of brewing. In the presence of unmodified corn cob, the caffeine concentrations were reduced by about 12±10%. The hydroxyl groups in cellulose probably interacted with caffeine, which is schematically shown by Figure 4.4a.

Caffeine could bind with metal ions [31] and it was found in this work that modified corn cob incorporated with Na^+ and Ca^{2+} ions were able to remove more caffeine than unmodified corn cob was. Upon reacting with NaOH, the hydroxyl groups in cellulose were converted into oxy groups containing Na^+ ions as counter ions. An increase in hydrophilicity of adsorbent was favorable for the adsorption of caffeine. After 1 minute brewing, the caffeine concentration was reduced by 61% of the concentration in the solution without the adsorbent. The average reduction percent was 23±10 % since the 3 minute of brewing. Converting Na^+ ions to Ca^{2+} ions resulted in 59% of caffeine removal after 1 minute of brewing. However, the lower average reduction percent, 14±10 %, was observed from the adsorption for 3-20 minutes. The higher reduction percent achieved during the initial adsorption was because unoccupied adsorption sites were highly available. Ca^{2+}-form corn cob could adsorb less caffeine although there was a report that caffeine could interact with Ca^{2+} ions through its oxygen atoms [23]. This was probably because, based on the equal amounts of corn cob, more Na^+ ions could be incorporated with the adsorbent. A Ca^{2+} ion needed two hydroxyl groups while a Na^+ ion required only one hydroxyl group.

It was probable that caffeine bound with the ions by replacing a water molecule surrounding the ions. In aqueous solution, six water molecules formed a hydration shell around a Na^+ ion with their oxygen atoms pointing towards the ion while a Ca^{2+} ion was surrounded by eight water molecules [32]. The hydration shell of Ca^{2+} ion might give rise to the extraordinary stability. Possibly, it was difficult for caffeine to interact with the Ca^{2+} ion. Hypothetical interactions between caffeine and the ions are displayed by Figures 4.4b and 4.4c. Caffeine bound with ions through its O2 and O6 atoms [23]

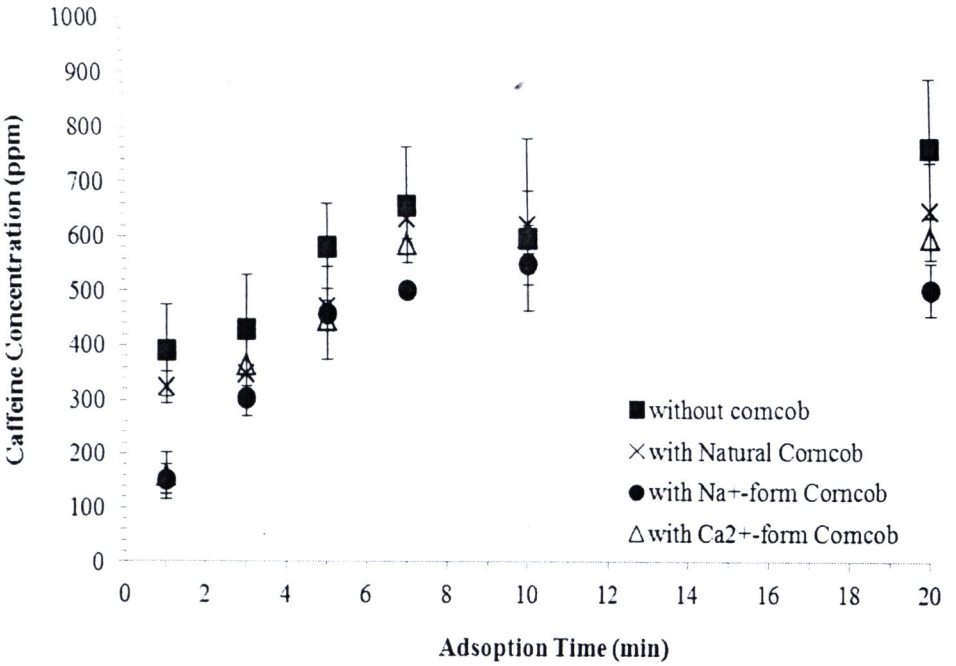
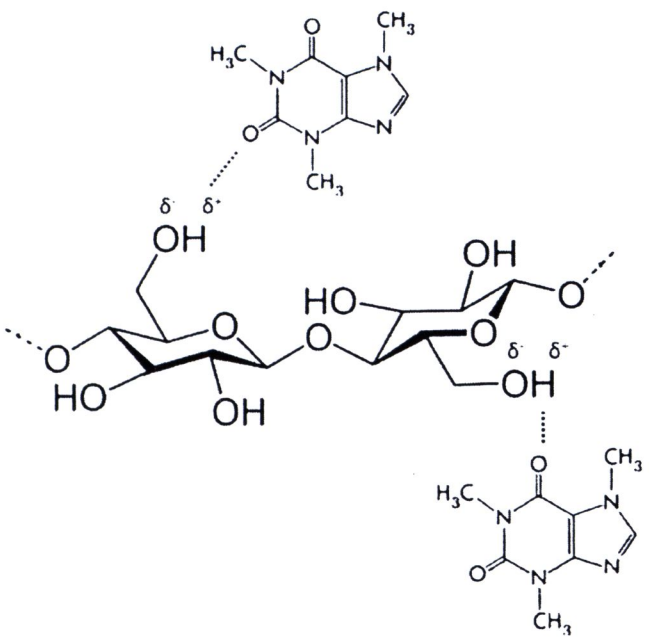


Figure 4.2 Caffeine concentrations in green tea solution of adsorption using different type corn cobs as the adsorbent.



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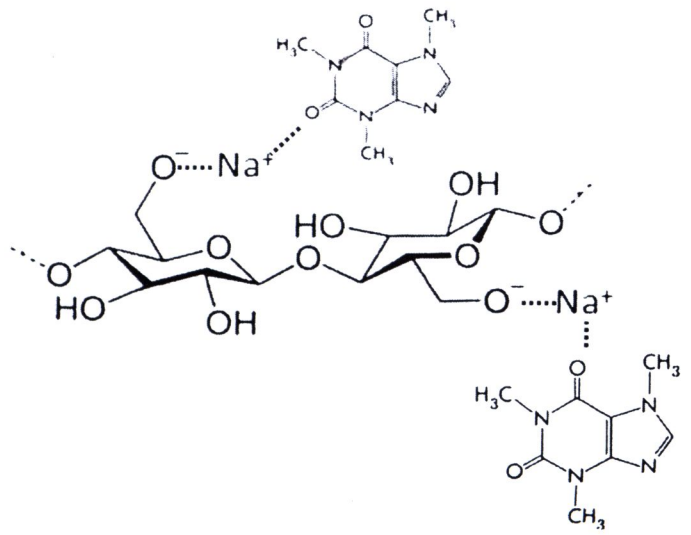

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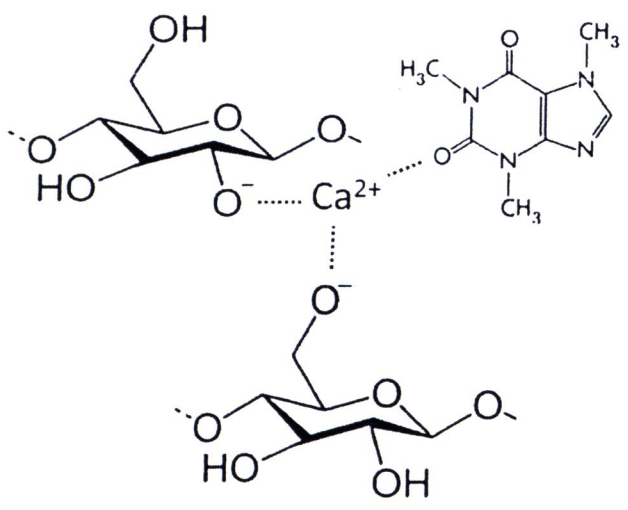

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Figure 4.3 Schematics of hypothetical interactions between caffeine and the ions (water molecules are omitted for clarity) (a) hydroxyl group (b) Na^+ ions (c) Ca^{2+} ions.

Natural corn cob did not exhibit polyphenol adsorption ability. Polyphenol concentrations of the green tea solution without any adsorbent were roughly the same as those with the unmodified corn cob as presented by Figure 4.5. This was partly because corn cobs also contained polyphenols, providing additional polyphenols to the green tea solution. Polyphenol concentration of about 76.73±5 ppm was obtained from boiling natural corn cob in 80 °C water for 1 minute. It remained unchanged for 20 minutes.

The increase in hydrophilicity of corn cob resulted in the reduction in polyphenol concentration. The adsorbents adsorbed polyphenols in the same manner as caffeine, i.e. the high reduction percents were obtained at the beginning of adsorption. By using modified corn cob in Na^+ and Ca^{2+} forms, the average polyphenol concentrations after 1 minute adsorption was 570 ppm, a 58% reduction, and 488 ppm, a 64% reduction, respectively. The less reduction percent, 27±17%, was obtained for the adsorption during the 3 and 20 minute by modified corn cob in Na^+ form. Likewise, modified corn cob in Ca^{2+} form could decrease polyphenol concentration by 25±22%. Adsorptions of polyphenols by the modified corn cobs were probably through the interactions between oxygen atom of polyphenol hydroxyl group, which was slightly negative, and the cations.

Lastly, the ratio of polyphenol concentration to caffeine concentration was about 3.32±0.2 irrespective of adsorbent, while it was 3.24 in the absence of adsorbent. Base on recommended maximum caffeine consumption of 300 mg per day [33] and 1 minute brewing time, 929, 1961 and 1887 ml of green tea per day can be consumed if unmodified, Na^+ form and Ca^{2+} form corn cobs are used, respectively. 767 ml per day can be taken if the adsorbent was not used.

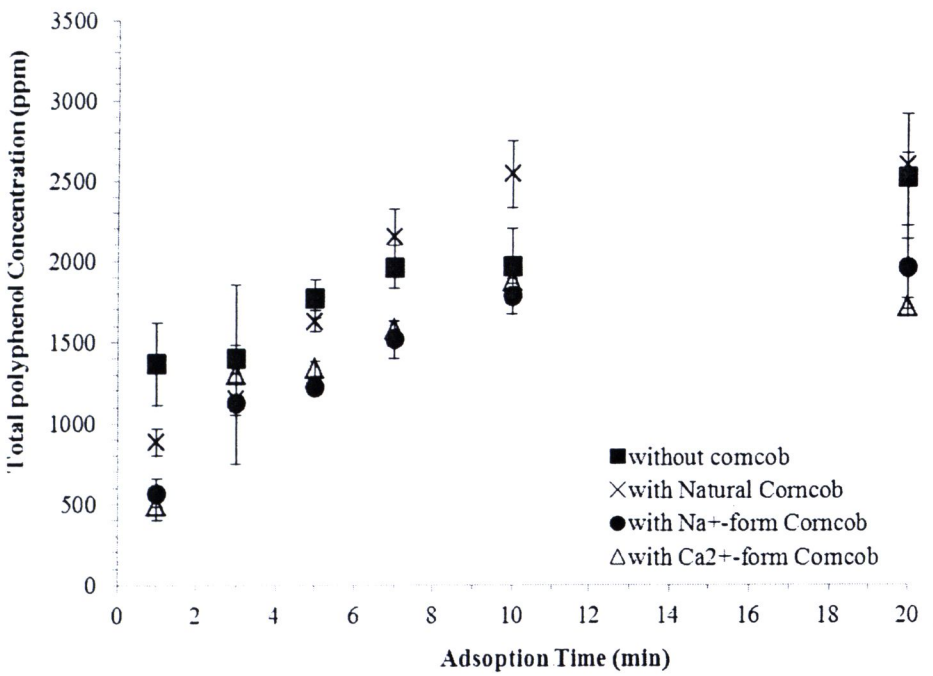


Figure 4.4 Total polyphenol concentrations in green tea solution of adsorption using different type corn cobs as the adsorbent.

4.3 Adsorption of green tea using corn cobs in tea bag

2 grams of green tea were brewed in a tea bag at 80 °C. Size of the tea bag was 5 × 8 cm^2. The adsorbents were unmodified and modified corn cobs incorporated with Na^+ and Ca^{2+} ions.

4.3.1 Effect of functional group on adsorption ability

Tannin is an astringent compound, causing bitterness in green tea. It was reported that the acceptable tannin concentration in green tea was 200 mg/L [34]. From the result shown by Figure 4.6, brewing green tea in tea bag longer than 7 minutes led to the unacceptable tannin concentration. After 7 minutes, the tannin concentration was 229 mg/L.

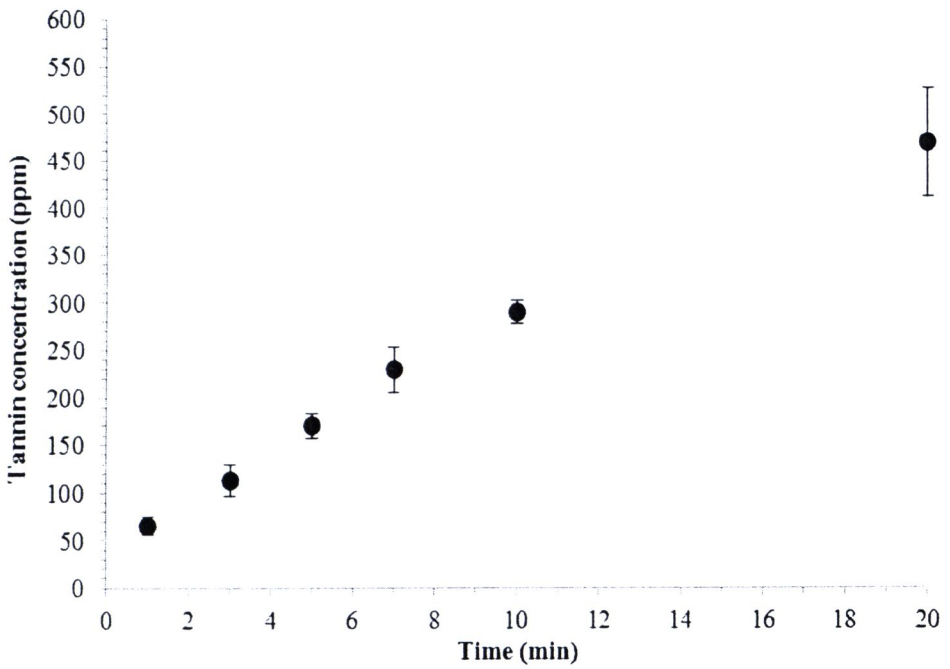


Figure 4.5 Tannin concentrations in green tea solution.

With 2 grams of adsorbents in tea bag, tannin concentrations were lower than 200 mg/L although brewing time was longer than 7 minutes as shown by Figure 4.7. It was likely that the adsorption was attributed to interactions between hydrophilic moieties of the adsorbents and hydroxyl groups of tannin. The adsorption by unmodified corn cob was a result of hydrogen bondings between its hydroxyl groups and those of tannin. Because of higher hydrophilicity of oxy groups, the modified corn cobs were able to remove tannin to lower concentrations.

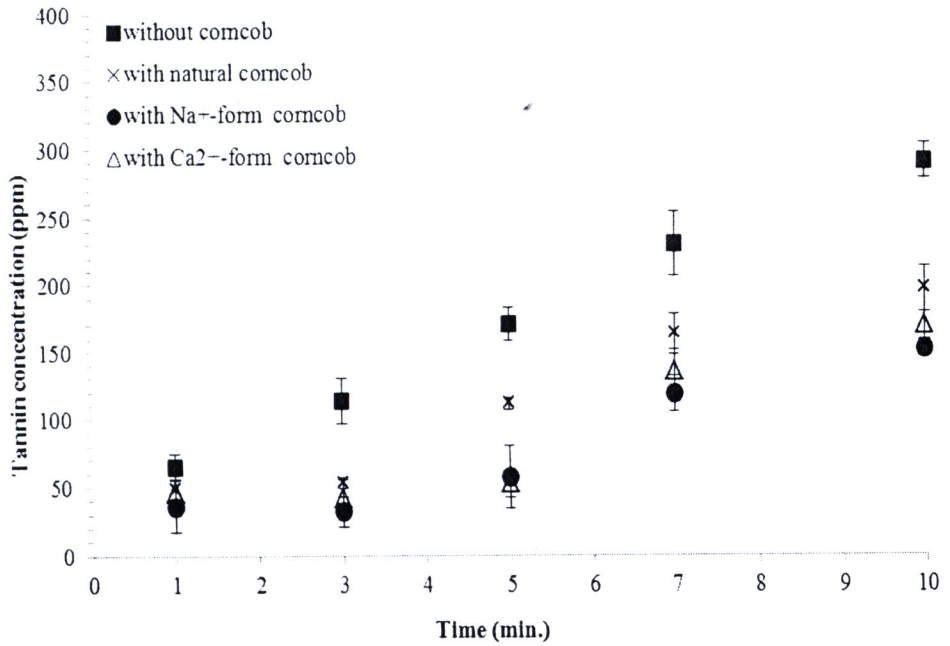


Figure 4.6 Tannin concentrations in green tea solution of adsorption using different type corn cobs as the adsorbent.

The adsorption of caffeine and polyphenolic compounds using unmodified and modified corn cobs (The ratio of green tea:corn cobs was 2:2) at 80 °C were discussed in this section. Caffeine was not detected after 1 minute of brewing because it must permeate through tea bag. Another possible explanation was that caffeine was scarcely extracted due to limited amounts of water, which was caused by the ability of corn cob to adsorb water.

Like tannin, caffeine could be more adsorbed by the modified corn cob as shown by Figure 4.8. There were reports about interaction between cellulose and caffeine [2, 3], it was possible that hydrophilicity of caffeine played a role in caffeine adsorption by unmodified corn cob. The average reduction percents from the 3 to 10 minute were 32, 71 and 62 for unmodified, Na^+ form and Ca^{2+} form corn cobs respectively. These were higher than caffeine reduction percents obtained without a tea bag. A plausible explanation was that caffeine was confined within a tea bag, providing the higher concentration and, therefore, adsorption driving force.

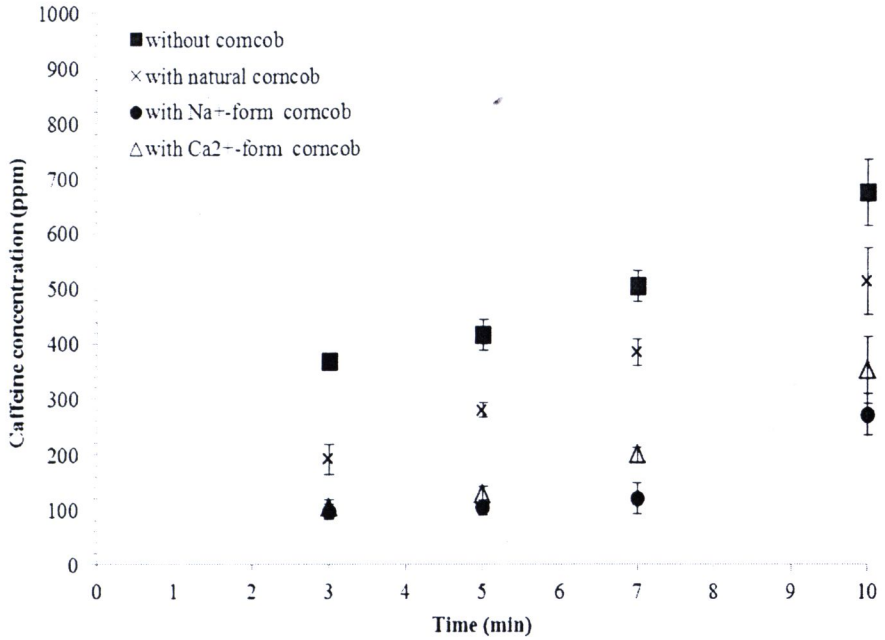


Figure 4.7 Caffeine concentrations in green tea solution of adsorption using different type corn cobs as the adsorbent.

Figure 4.9 showed total polyphenol concentrations in green tea infusions for the period of 1-10 min. Unlike the adsorption without tea bag, polyphenols were adsorbed by natural corn cob due to hydrogen bonding between hydroxyl groups of polyphenol and natural corn cob. The concentration was reduced by an average of 35%. Further reductions, 73% by Na^+-form and 67% by Ca^{2+}-form corn cobs, were caused by the increase in hydrophilicity of the adsorbents.

Finally, the ratio of polyphenol concentration to caffeine concentration was about 2.65±0.2 irrespective of adsorbent, while it was 2.58 in the absence of adsorbent. These ratios were lower than those obtained from the experiments without tea bag. Competitive permeation of polyphenol and caffeine through tea bag was responsible for the lower ratios. Polyphenols were larger than caffeine and permeated slower through a tea bag. If green tea was brewed for 3-10 min by unmodified, Na^+-form and Ca^{2+}-form corn cobs, 870, 2020 and 1530 ml of green tea, respectively, could be consumed each day and less than 300 mg of caffeine would be taken.

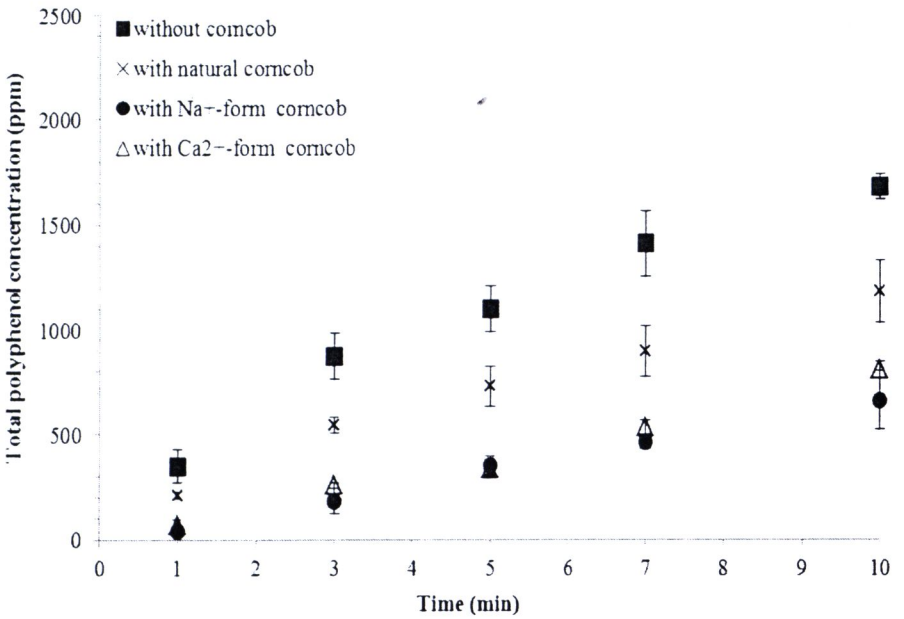
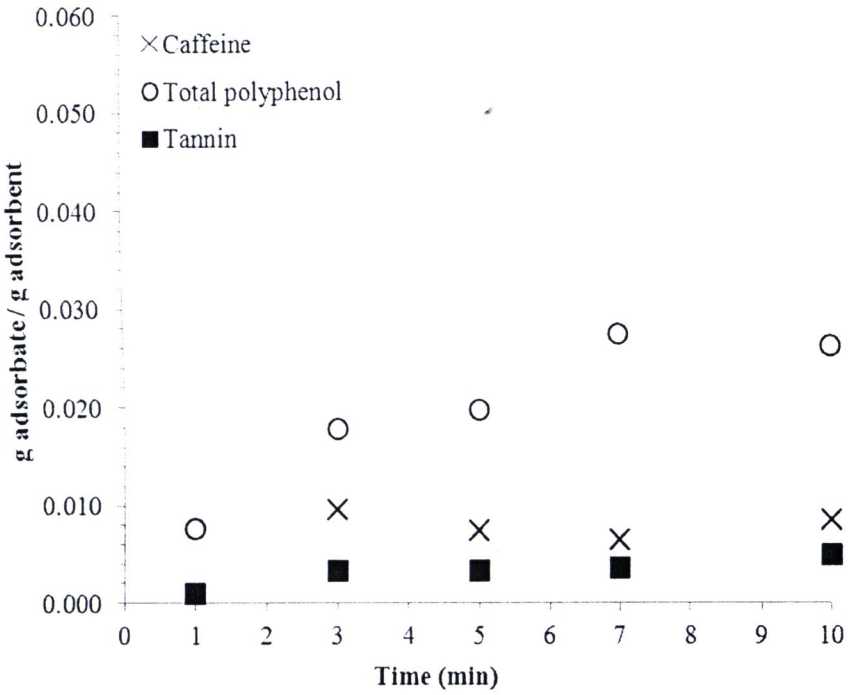


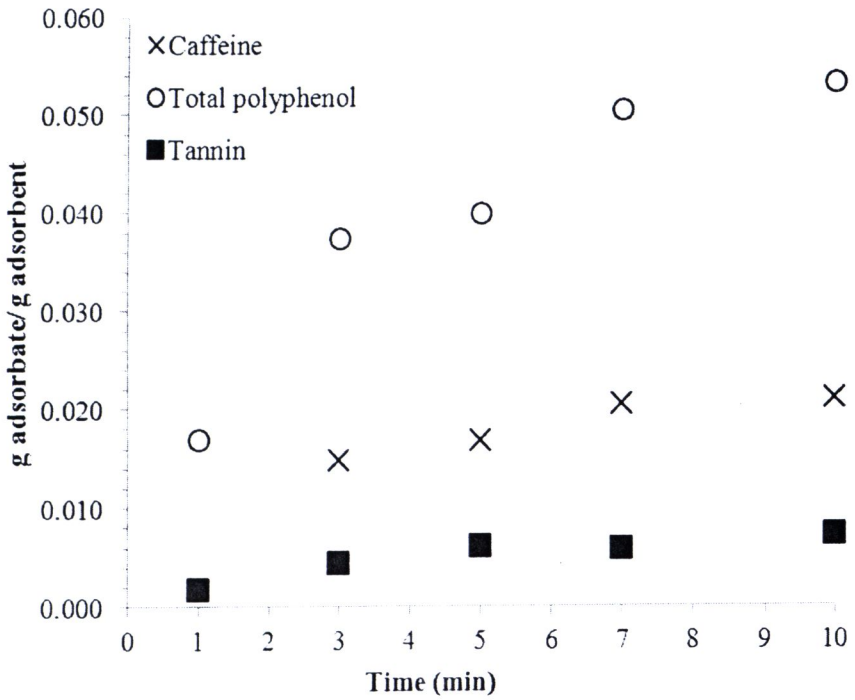
Figure 4.8 Total polyphenol concentrations in green tea solution of adsorption using different type corn cobs as the adsorbent.

4.3.2 Effect of green tea leave to adsorbent mass ratio

Adsorption capacity of every adsorbent was in the descending order: polyphenols > caffeine > tannin as presented by Figure 4.10. The maximum caffeine adsorption capacity was reached since the third minute of adsorption. In contrast, adsorption capacities of polyphenols and tannin initially increased and subsequently leveled off, indicating that adsorption sites were completely occupied.


0.060
0.050
0.040
0.030
0.020
0.010
0.000
g adsorbate / g adsorbent
×Caffeine
OTotal polyphenol
■Tannin
0 1 2 3 4 5 6 7 8 9 10
Time (min)

a


0.060
0.050
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0.000
g adsorbate/ g adsorbent
×Caffeine
OTotal polyphenol
■Tannin
0 1 2 3 4 5 6 7 8 9 10
Time (min)

b

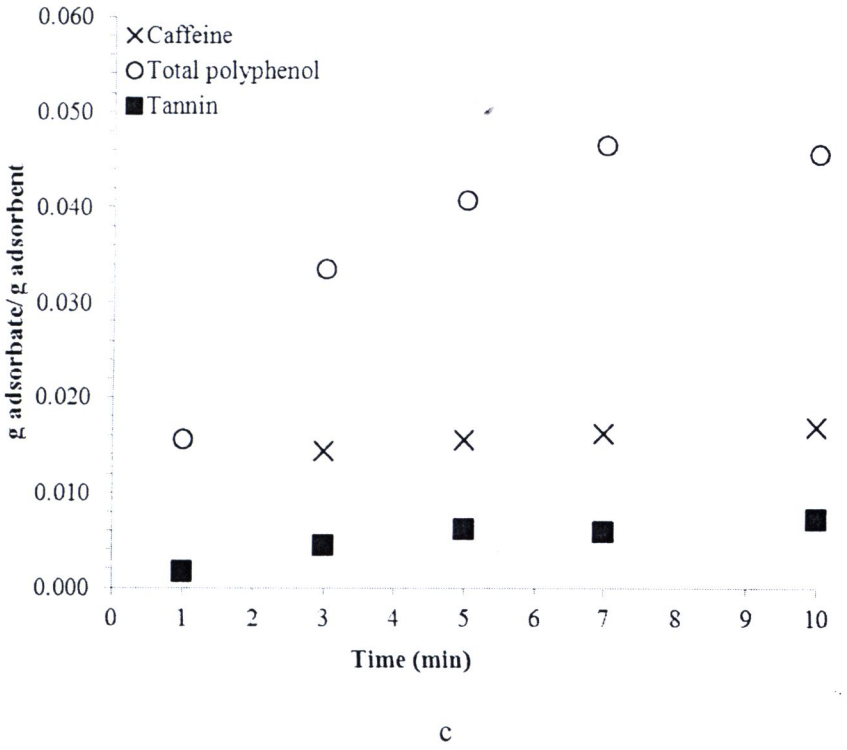
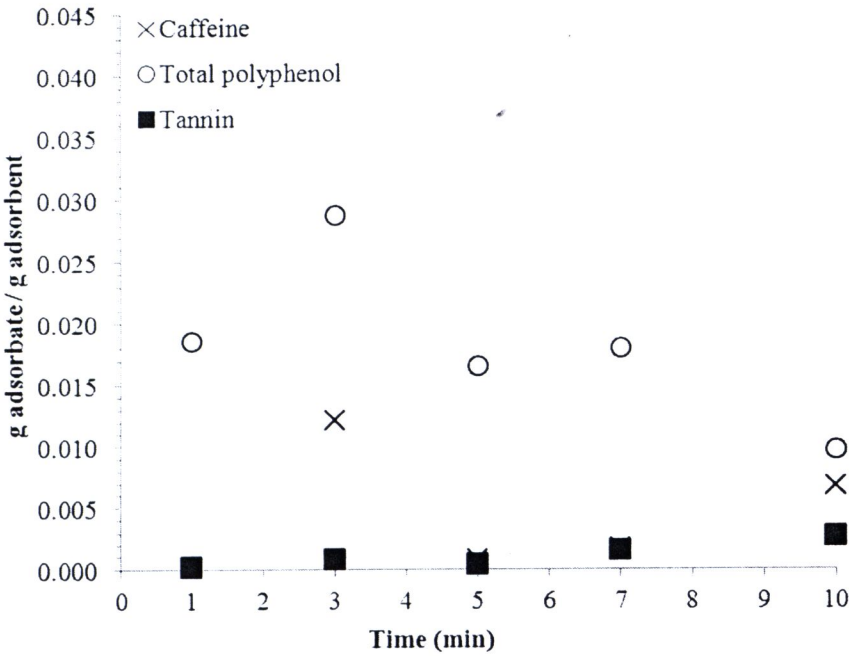
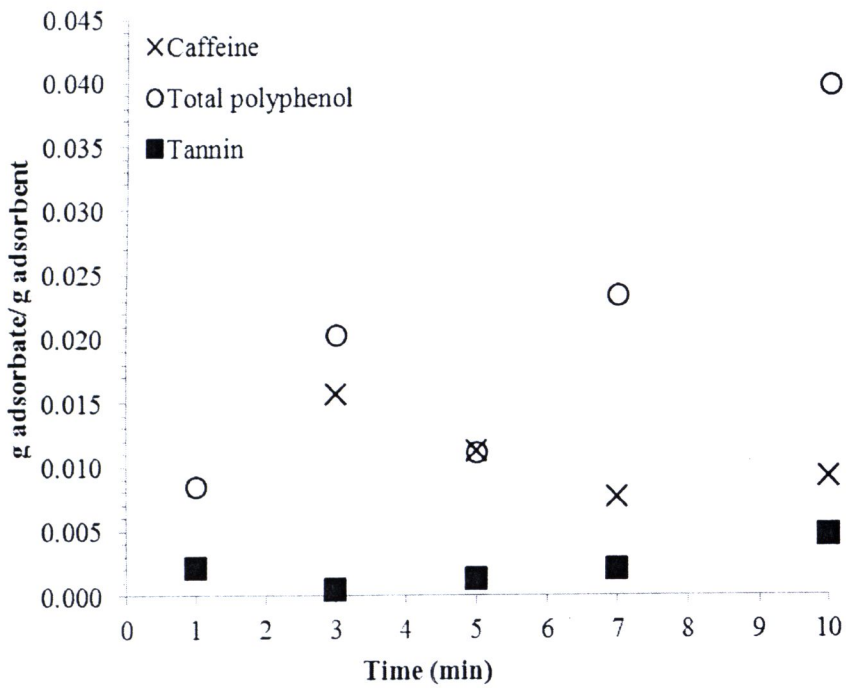


Figure 4.9 Mass of adsorbate per unit mass of adsorbent using green tea to corn cobs mass ratio of 2:2 (a) natural corn cob (b) Na^{+}-form corn cob (c) Ca^{2+}-form corn cob.

As the mass of adsorbents were reduced, the adsorption capacities became less for the most part although they should have been the same as those observed when the mass was 2 grams. The reasons were not known. Furthermore, the data were also scattered.


0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
g adsorbate/ g adsorbent
×Caffeine
○Total polyphenol
■Tannin
0 1 2 3 4 5 6 7 8 9 10
Time (min)

a


0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
g adsorbate/ g adsorbent
×Caffeine
○Total polyphenol
■Tannin
0 1 2 3 4 5 6 7 8 9 10
Time (min)

b

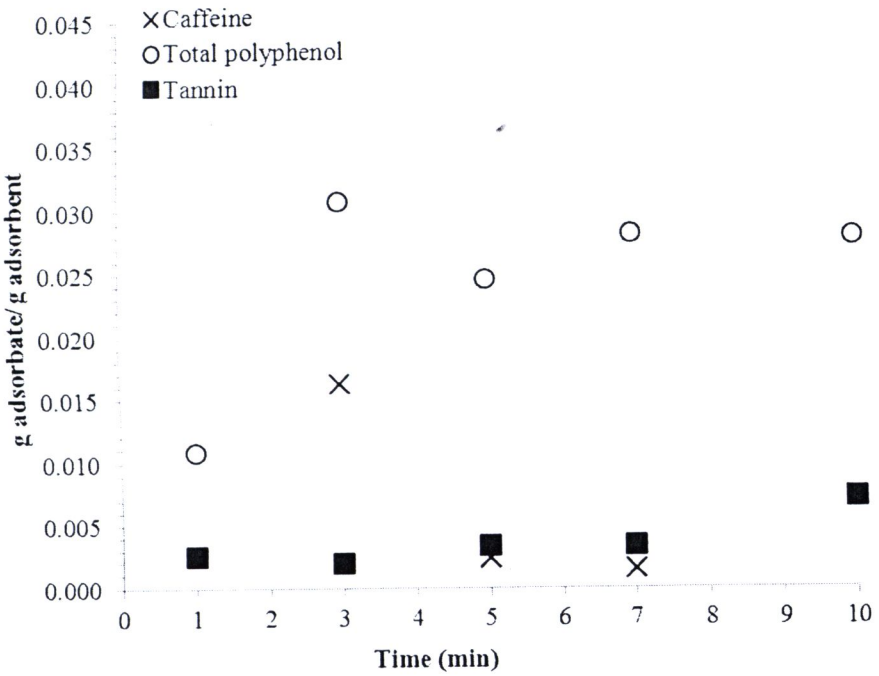


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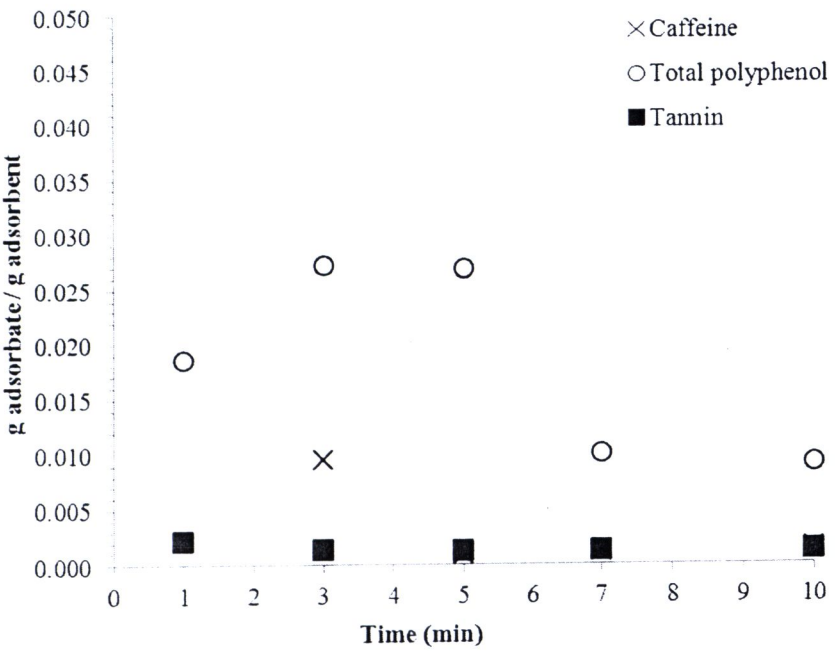
Figure 4.10 Mass of adsorbate per unit mass of adsorbent using green tea to corn cobs mass ratio of 2:1 (a) natural corn cob (b) Na^{+}-form corn cob (c) Ca^{2+}-form corn cob.



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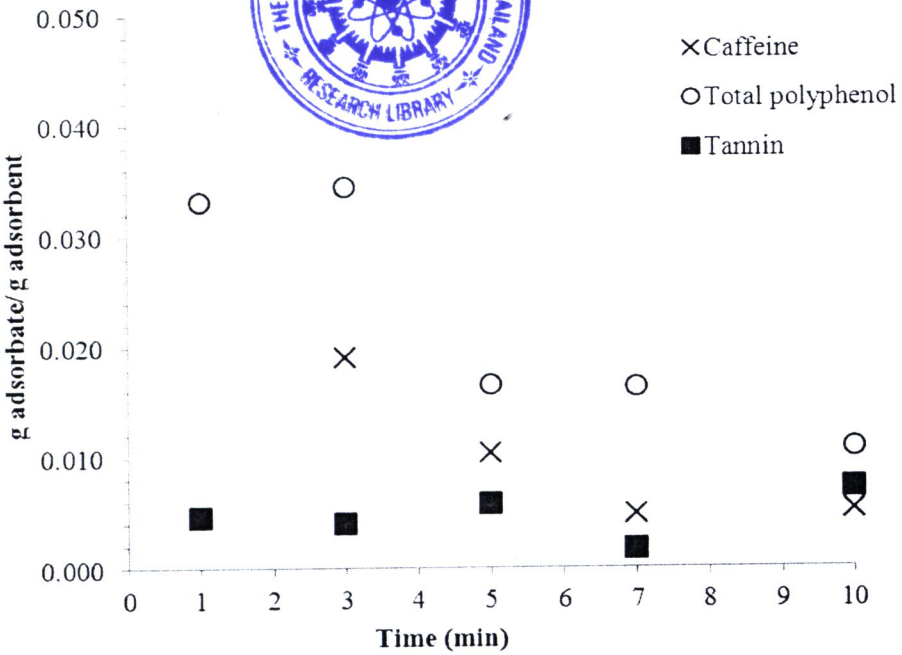

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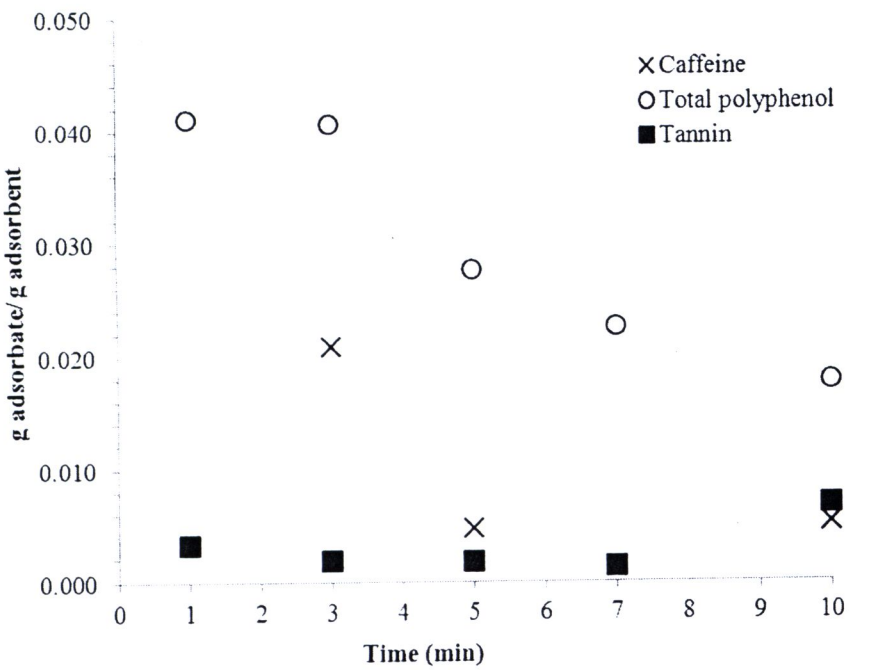

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Figure 4.11 Mass of adsorbate per unit mass of adsorbent using green tea to corn cobs mass ratio of 2:0.5 (a) natural corn cob (b) Na^{+}-form corn cob (c) Ca^{2+}-form corn cob.