Assessment of Isothermal Alkaloid Adsorption in Cigarettes by Low Cost Adsorbents

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Abstract

This work estimates the capacity of six low cost adsorbents (Sawdust, bagasse, green tea leaves, coconut fiber, neem bark and green tea waste) in removal of harmful constituents from mixture of alkaloids in tobacco extract. Tobacco solution used for the purpose was from five brands of cigarettes i.e., Moments, capstan, goldflake, tambaku and bidi, which are very common among people of India. To model the experimental data two of the very common isotherm model Langmuir isotherm model and the Freundlich isotherm model have been implemented. The study revealed that green tea waste and green tea leaves showed maximum capacity of adsorption thus proved to be better adsorbents as compared to other four adsorbents.

Keywords: Alkaloids, Langmuir isotherm, Freundlich isotherm, low cost adsorbents, cigarettes, extract, tobacco

Introduction

Tobacco includes any plant of the genus Nicotiana of the nightshade family (Solanaceae). Cultivated tobacco (Nicotiana tabacum) is the most widely planted species and is grown worldwide for the production of tobacco leaf. The presence of alkaloids, such as nicotine, nornicotine, anabasine, and anatabine, is characteristic of Nicotiana species. The chemical composition of tobacco leaves is extremely complex, with one alkaloid, nicotine, being the most characteristic constituent of tobacco and responsible for its addictive nature **(1)**. Therefore, the composition and content of alkaloids in leaves are critical to tobacco quality **(2)**. However, some types of alkaloids including nornicotine and myosmine, have adverse effects on human health **(3, 4, 5, 6)**. Nornicotine is a biochemical precursor of N′-nitrosonornicotine, a tobacco-specific nitrosamine that has been shown to exhibit carcinogenic properties in laboratory animals **(5)**. In addition, upon nitrosation, myosmine can yield 4-hydroxy-1-(3-pyridyl)-1-butanone and N′-nitrosonornicotine, which are strong carcinogens **(4)**. Currently, there is no efficient approach for selectively reducing the amount of harmful alkaloids in tobacco leaves.

Using tobacco is one of the leading preventable causes of disease and premature death worldwide. Tobacco use contributes in 10 global deaths and is the second major cause of mortality in the world **(7, 8).** There are approximately 1.25 billion smokers in the world representing about a third of the adult global population; 800 million of these people live in developing countries. While the cigarette consumption has been increased in most of the developing countries, the past 25 years has been marked by a steady decline in cigarette consumption in some developed countries. However the world cigarette production has increased about four times during the last 50 years **(9,10,11,12,13).** It has been reported that to date, more than 3000 chemicals have been isolated from tobacco which more than 1000 of these chemical constituents present in unburnt **(14, 15)**.

Adsorption is considered to be one of the most effective technologies widely used in global environmental protection areas. The performance of an adsorbent can be studied by adsorption isotherm data, which can be obtained by a series of experimental tests in labs. Modeling the adsorption isotherm data is an essential way for predicting and comparing the adsorption performance, which is critical for optimization of the adsorption mechanism pathways, expression of the adsorbents capacities, and effective design of the adsorption systems **(16)**. Several two-parameter isotherm models are commonly used in modeling the adsorption data, such as Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich et al. **(17,18, 19, 20).** In general, the modeled adsorption isotherm is an invaluable non-linear curve describing the adsorption phenomenon at a constant temperature and pH; and the mathematical correlation which is depicted by the modeling analysis is important for operational design and applicable practice of the adsorption systems **(21)**. On the other hand, linear analysis of isotherm data into isotherm models is an alternative mathematical approach to predict the overall adsorption behavior.

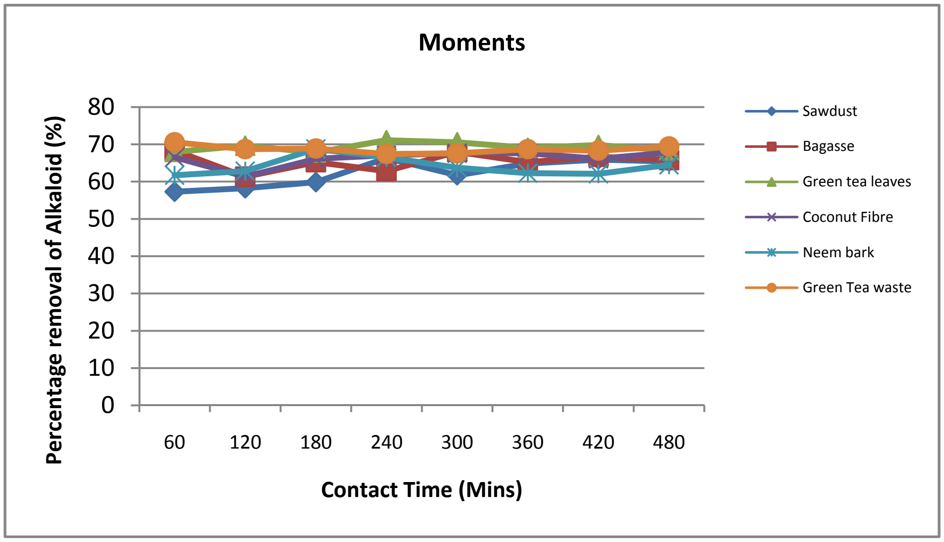
This work assesses the alkaloid adsorption capacity of six low cost adsorbents i.e. Sawdust, bagasse, green tea leaves, coconut fiber, neem bark and green tea waste. Five brands of cigarettes i.e., Moments, capstan, goldflake, tambaku and bidi, which are commonly used among people of India, were targeted to determine their alkaloid contents. The effect of adsorbents in reducing the content of harmful alkaloids from total alkaloids would help to minimize its detrimental consequences on human health.

Materials and Methods:

The adsorbents used for the adsorption study low cost, they include used-Sawdust, bagasse, green tea leaves, coconut fibre, neem bark and green tea waste. The alkaloid extracts were prepared from tobacco of five Indian brand cigarettes which are popularly used by both lower and upper class people. They were Moments, Goldflake, Capstan, Tambaku and Bidi. The method followed was same as mentioned in our earlier work. The adsorbents were collected, washed and dried at 80OC. After complete removal of moisture, the adsorbents were grinded in electrical grinder and sieved to obtain uniform particle. These powdered adsorbents were then stored in the air tight bottles. For each brand, the tobacco was removed from the wrapping, weighed, and pooled for extraction with methanol. A part of extract residue was dissolved in 2N HCL and then filtered. 1 ml of this solution was transferred to separatory funnel and washed with 10 ml chloroform (3 times). The pH of this solution was adjusted to neutral with 0.1 N NaOH. Then 5 ml of BCG solution and 5 ml of phosphate buffer were added to this solution. The mixture was shaken and complex extracted with 1, 2, 3 and 4 ml chloroform by vigorous shaking, the extract was then collected in a 10 ml volumetric flask and diluted with chloroform. The absorbance of the complex in chloroform was measured at spectrum of 470 nm in UV-Spectrophotometer (UV-Vis Double Beam Spectrophotometer) against the blank. The major emphasis of each adsorbent material is on its adsorption capacity. Two isotherm models were followed here to assess the adsorption capacity of each low cost adsorbent from the alkaloid extract. These two isotherm models are: the Langmuir isotherm model **(22)** and the Freundlich isotherm model **(23)**.

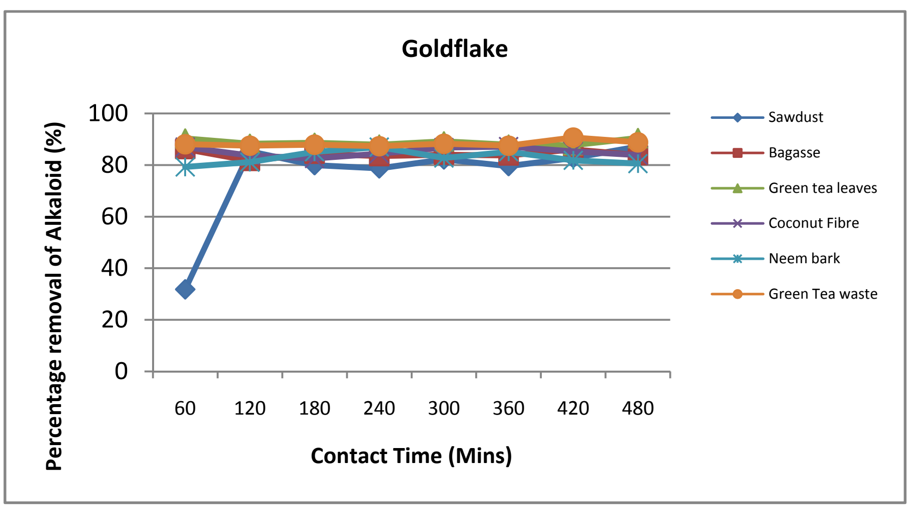
Result and Discussion

As depicted in Graph (1-5), the percentage removal of alkaloids, from the methanolic extracts of tobacco from cigarettes (Moments, capstan, goldflake, tambaku and bidi) with the help of low cost adsorbents (Sawdust, bagasse, green tea leaves, coconut fiber, neem bark and green tea waste). The figures show the relationship between removal of alkaloids and their contact time with the alkaloid extract. The time duration of experimental setup was ranging from 60 min to 480 mins.



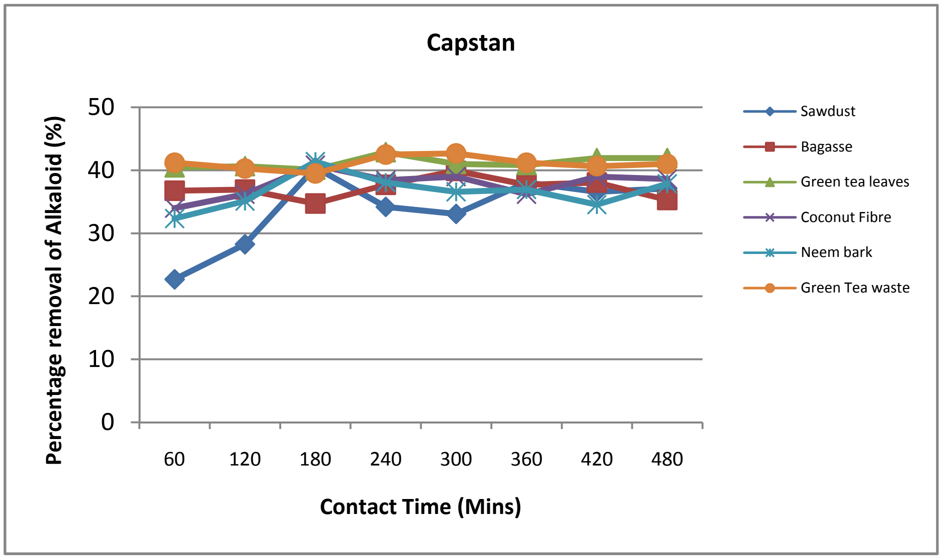
Graph 1: Percentage removal of alkaloids in moments cigarettes extracts by different low cost adsorbents

As observed in figure 1, all the six adsorbents showed nearly similar percentage removal of alkaloid from the methanolic extract of moments cigarettes. But out of six adsorbents, the highest was seen with green tea leaves at percentage of 71.13 at 240 mins, followed by green tea waste (70.58%) at 60 mins, neem bark (68.80%) at 180 mins, bagasse (68.37%) at 60 mins, coconut fiber (67.63%) at 240 mins and sawdust (66.34%) at 60 mins. On the other hand, minimum adsorption capacity was seen with bagasse and coconut fibers of 61.36% at 120 mins, others varying from 61.73% (neem bark), 65.42% (sawdust), 67.45% (green tea waste) and 67.82% (green tea leaves) at 60 mins,480 mins, 240 mins and 180 mins respectively.



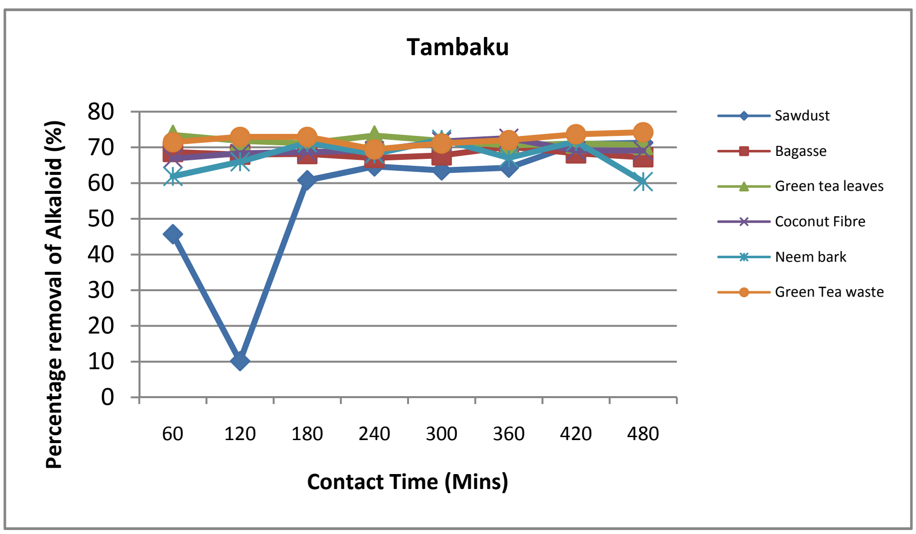
Graph 2: Percentage removal of alkaloids in Goldflake cigarettes extracts by different low cost adsorbents

In figure 2, the alkaloid removal from goldflake methanolic extract with the help of six adsorbents has been shown. Green tea waste has shown best result among six adsorbents as in the case of moments cigarettes. Lowest percentage was seen at 240 min (87.36%) which elevates to 90.68 % as the contact time increased to 420 mins. A similar increase was observed in case of four adsorbents. Sawdust lowest percentage removal was of 31.82% at 60 mins which increased upto 85.34% at 120 mins. Green tea leaves from 87.73 (420 mins) to 90.49% (480 mins), coconut fibre from 82.58 % (180 mins) to 87.18% (360 mins) and neem bark 79.27% (60 mins) to 87.0 % (240 mins).



Graph 3: Percentage removal of alkaloids in Capstan cigarettes extracts by different low cost adsorbents

In figure 3, the variation in percentage removal of alkaloid from capstan cigarette methanolic extract using six different adsorbents have been demonstrated. In this case, green tea leaves showed better capacity of adsorbtion than green tea waste. An increase in contact time of the adsorbent with the alkaloid solution, increase percentage removal of alkaloids as observed in all the cases in as observed in figure 3. Sawdust from 22.7% to 40.47%, bagasse from 34.74% to 39.92, green tea leaves from 40.10 % to 42.88%, coconut fiber from 34.0% to 40.84%, neem bark from 32.34% to 41.40 and green tea waste from 39.5% 42.69%.



Graph 4: Percentage removal of alkaloids in Tambaku cigarettes extracts by different low cost adsorbents

In figure 4 and 5, the percentage removal of alkaloid from tambaku and bidi extract has been presented. In case of tambaku, green tea waste showed highest removal with 74.25% at 480 min followed by green tea leaves (73.51%), cocnut fiber (72.59%), neem bark (71.67%), sawdust (71.34%) and bagasse (70.20%) whereas in case of Bidi, a sudden rise of adsorption capacity of sawdust was observed with 86.91% removal at 60 min and then decline as the contact time increased. While other adsorbents have shown similar results and value obtained were in range of 13-14%. Green tea maximum percentage was seen at 480 min with 14.23% and minimum at 240 min (13.81%), Neem bark maximum percentage was seen at 180 min with 14.10% and minimum at 60 min (13.13%), Coconut fiber maximum percentage was seen at 360 min with 13.90% and minimum at 120 min (13.22%), green tea leaves maximum percentage was seen at 480 min with 13.96% and minimum at 60 min (13.88%), Bagasse maximum percentage was seen at 240 min with 13.98 % and minimum at 120 min (13.28%),

Graph 5: Percentage removal of alkaloids in Bidi cigarettes extracts by different low cost adsorbents

The adsorption isotherms of alkaloids from the cigarette extract onto low cost adsorbents at varying time duration has been shown in the figures below (Figure 6 [a-d] & Figure 7 [a-d]). Equilibrium data (adsorption isotherms) are required for designing of adsorption systems **(24).** Here, the equilibrium data for alkaloid extract on low cost adsorbents have been modelled with the Langmuir and Freundlich models. As it can be seen from the results presented in figure 6 and 7, the adsorption isotherms of alkaloid onto low cost adsorbents are of the characteristic shape typical of isotherms at all of the investigated time durations with slight deviation in experimental data.

Langmuir Isotherms

The **Langmuir (22)** isotherm relationship is of a hyperbolic form:

$q_e = q_{max}\, bc_e / 1 + bc_e$

The Langmuir relationship can be linearized by plotting either $(1/q_e)$ vs $(1/\mathbf{C}f)$ or $(\mathbf{C}f/q_e)$ vs $\mathbf{C}f$

$1/q_e = 1/c_e(1/q_{max}\, b) + (1/q_{max})$

q_{max} and ***b*** can be determined from the linear plot of $1/q_e$ versus $1/c_e$

Where:

q_{max} is the maximum sorbate uptake under the given condition **b** is a coefficient related to the affinity between the sorbent and sorbate.

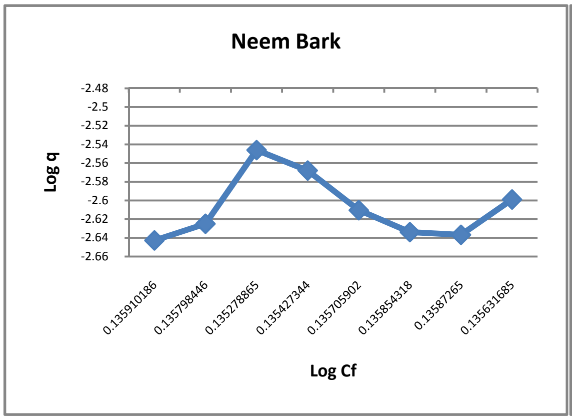
Freundlich's Model:

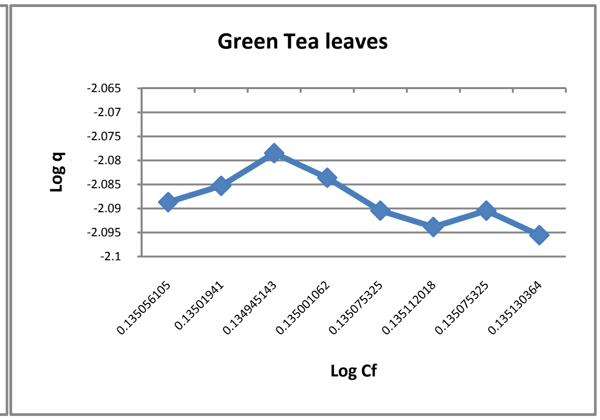
This isotherm also considers monolayer sorption with a heterogenous distribution of active sites of the sorbent **(23)**.

The **Freundlich** isotherm relationship is exponential:

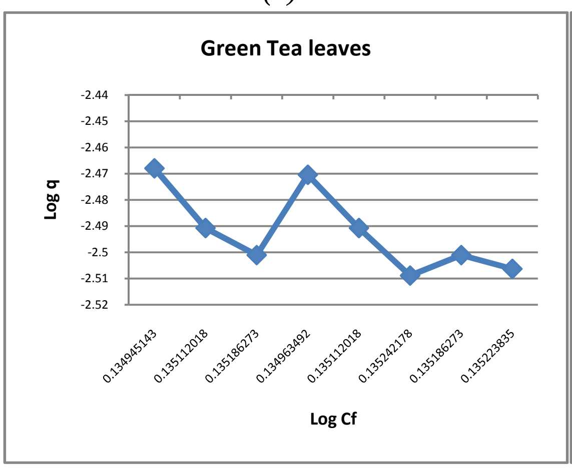
$q = k_f \ c_f^{\ 1/n}$

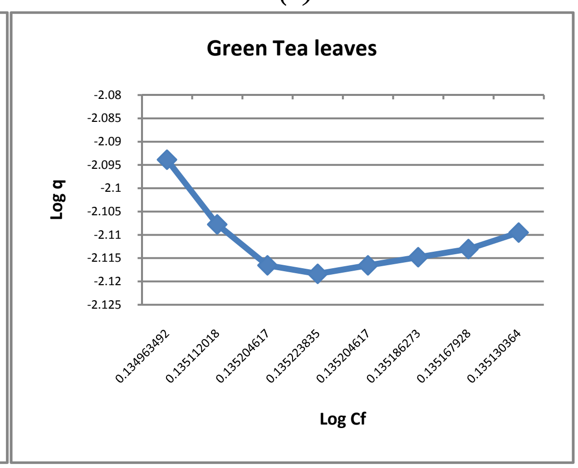
Where: **k** and **n** are Freundlich constants.





(a) *(b)*





(c) *(d)*

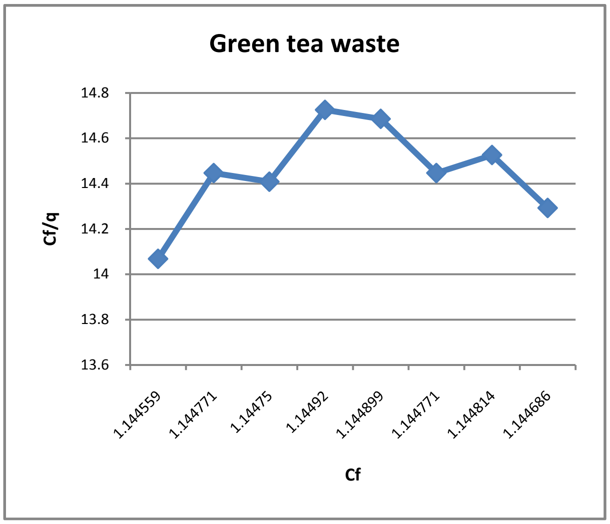
Graph 6: Freundlich Isotherm for alkaloid adsorption capacity of low cost adsorbents in variable time duration (a) alkaloid adsorption capacity of Neem bark from Moments cigarette methanolic extracts (b) alkaloid adsorption capacity of green tea leaves from capstan cigarette methanolic extracts (c) adsorption capacity of green tea leaves from tambaku methanolic extracts (d) alkaloid adsorption capacity of green tea leaves from Bidi methanolic extracts

The Freundlich relationship is an empirical equation. It does not indicate a finite uptake capacity of the sorbent and can thus only be reasonably applied in the low to intermediate concentration ranges (**$C_{f!}$**). However, it is easier to handle mathematically in more complex calculations (e.g. in modeling the dynamic column behavior) where it may appear quite frequently. Freundlich model can be easily linearized by plotting it in a (log-log) format.

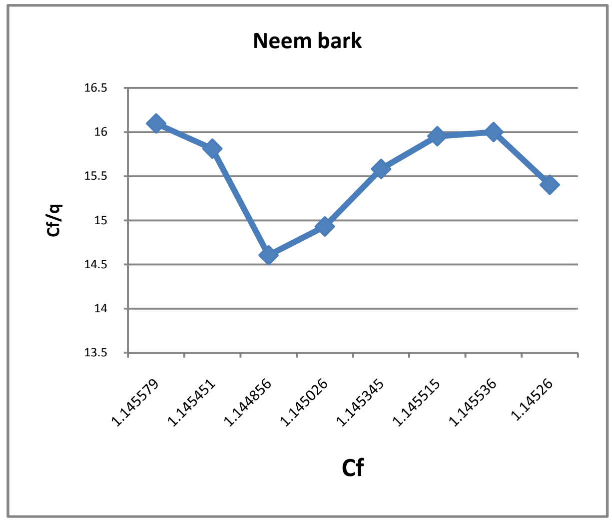
$\text{Log } q = \log (k_f \, cf^{\ 1/n})$

The Langmuir model has eventually been empirically most often used since it contains the two useful and easily imaginable parameters ($\mathbf{q_{max}}$ and **b**) which are more easily understandable since they reflect the two important characteristics of the sorption system.

From the above interpretation, it was deduced that green tea waste has maximum capacity of adsorption of harmful constituents from aqueous solution of alkaloid extract. It was also seen, that higher the contact time of adsorbent with the extract, more is the percentage removal of alkaloid except in few cases where as the time increased, removal starts reducing gradually. Thus best result among six adsorbents was foe green tea was followed by green tea.



(a)



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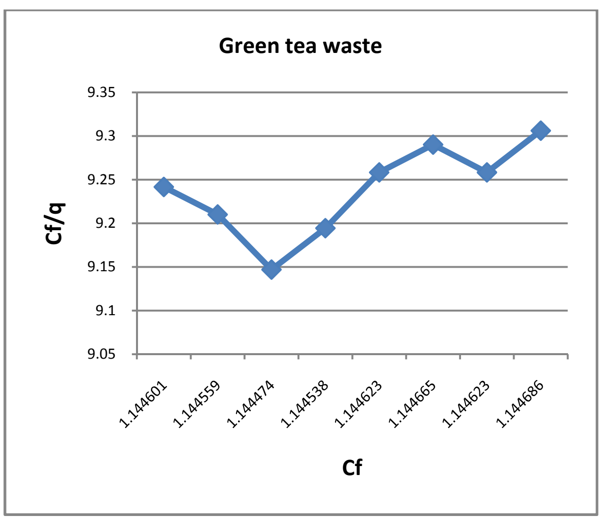
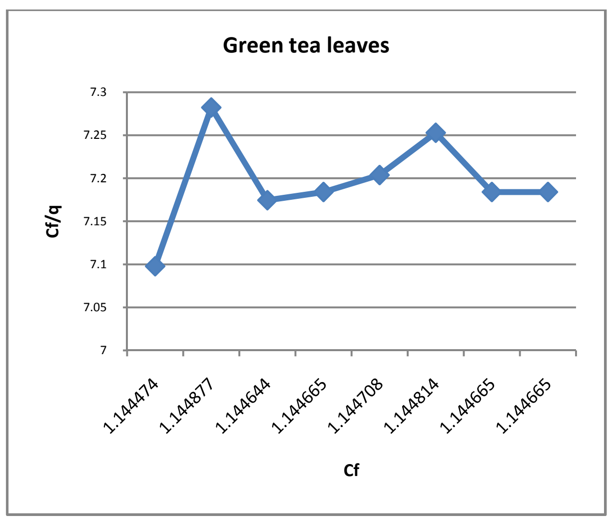


(c)



(d)

Graph 7: Langmuir Isotherm for alkaloid adsorption capacity of low cost adsorbents in variable time duration (a) alkaloid adsorption capacity of Green tea waste from moments cigarette extracts (b) alkaloid adsorption capacity of Neem bark from moments cigarette extracts (c) alkaloid adsorption capacity of Green tea waste from Capstan extracts (d) alkaloid adsorption capacity of Green tea leaves from moments extracts

Conclusion

The findings revealed that green tea leaves and green tea waste were two best adsorbents for the alkaloid solution. In case of moments cigarettes, the highest alkaloid removal was seen with green tea leaves at percentage of 71.13 at 240 mins, followed by green tea waste (70.58%) at 60 mins, In goldflake, green tea waste has shown best result with 90.68 % at 420 mins. In capstan cigarette case, green tea leaves showed better capacity of adsorbtion than green tea waste. An increase in contact time of the adsorbent with the alkaloid solution increased percentage removal of alkaloids. Green tea leaves from 40.10 % to 42.88% was observed. In case of local tobacco i.e., tambaku, green tea waste showed highest removal with 74.25% at 480 min followed by green tea leaves (73.51%) and another local cigarette, bidi had a deviation in result with sawdust showing maximum capacity with 86.91% removal at 60 min and then decline as the contact time increased. This study confirmed that green tea leaves and green tea waste as low cost adsorbent could be employed for the removal of alkaloid and thus reduce the harmful effect of cigarettes.

Acknowledgment

I am highly indebted to my advisor Dr. Amit Chattree for his guidance and constant supervision as well as for providing necessary information regarding the study. I express a heartfelt thanks to SHIATS, Allahabad for providing all the necessary facilities and support to complete this work.

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