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Comparative study of Neem (*Azadirachta indica*) leaf, bark and seed as an adsorbent for dye, methylene blue, removal

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Abstract
Adsorption is one of physiochemical approaches which can effectively be used for the removal of different pollutant in gaseous and liquid phases. Even though, different types of adsorbents are used for the removal of pollutant by the adsorption, activated carbon is frequently used as an adsorbent at industrial level due to its effective adsorptive capacity. However, the use of environmental friendly, naturally abundant and non-conventional adsorbents is becoming more popular for removal of pollutants since commercial adsorbents are quite expensive. Even though, several adsorption studies of Neem leaf powder have been reported, comparative study of adsorption by leaf, bark, seed coat and seed kernel has not been conducted. Therefore, in this study, it was attempted to evaluate the adsorption capacity of non-conventional adsorbents derived from Neem (*Azadirachta indica*) leaf, bark, seed coat and seed kernel compare their adsorption capacity and identify the adsorption mechanism using isotherm models. Four type of adsorbents were prepared using Neem leaf, bark, seed outer shell and seed kernel. The different plant parts were washed, dried (105°C) and powdered. The particle size less than 0.71mm was used as adsorbents for the study. Before the experiment, the characterization of adsorbents was performed. Methylene blue dye was used as the pollutant since it is frequent used dye for adsorption studies. Series of batch experiments were performed to evaluate the adsorption capacity of different adsorbents using different doses of adsorbents (1, 2 and 3g) and different initial adsorbate concentrations (50, 100, 150 and 200mg/L). One hundred milliliter of adsorbate in each concentration was taken into 250mL beaker and predetermined amount of adsorbent dose from each type was added, shaken in mechanical shaker (30min), allowed for settling. Then, adsorbate concentration in aqueous phase was determined using maximum absorbance wavelength (660nm) by a UV-visible spectrophotometer. Seed coat showed highest adsorption capacity of 87%. The adsorption capacity of leaf, bark and seed kernel was 83%, 80% and 69% respectively. Adsorption rate increases with adsorbent dose and decreases with increases of adsorbate initial concentration. Langmuir and freundlich isotherm were examined to understand the adsorption process. Langmuir isotherm showed high coefficient of determination more than 97% for all adsorbents except seed coat. Both Langmuir separation factor (R_L) and Freundlich constant (n_F) suggests the favorable adsorption of the dye onto the adsorbents. Adsorption process of all adsorbents except seed coat belongs to monolayer adsorption. Based on the study, it can be concluded that the adsorbents prepared for seed coat, bark and leaf can be used as an alternative adsorbent for the removal of pollutants from aqueous media.

Keywords: Adsorption, Isotherm, non-conventional adsorbents, Neem (*Azadirachta indica*), adsorption capacity

Introduction
Discharging wastewater without treatment is one of the major issues caused by industries. Due to the insufficient treatment of discharging wastewater, various environmental problems and health hazardous can be occurred. Wastewater mainly consists of three kind of pollutants namely organic, inorganic and biological pollutants. Biological, chemical and physical treatment methods are being used to remove the pollutants from the wastewater. Coagulation, flocculation, biodegradation, adsorption, membrane separation, ion exchange and oxidation are some of the techniques are frequently used (Khatod, 2013) [13]. Adsorption is a phenomena of attracting and retaining the molecules of a substance on the surface of liquid or a solid resulting into a higher concentration of the molecules on the surface. It is an effective method to eliminate pollutants from aqueous solution. The demand of non-conventional low-cost adsorbents increases due to the high cost of activated carbon. Neem (*Azadirachta indica*)

leaves can also be used as an alternative adsorbent. It has a good potential to eliminate the color from wastewater (Ghanshyam, 2013) [9]. Neem (*Azadirachta indica*) is in the Mahogany family Meliacea. It is native to India, Bangladesh, Nepal, Pakistan and Sri Lanka. It suits for tropical or semi tropical region. It contains volatile components for instance, azadirachhtin, etc., that is highly beneficial due to their properties like antibacterial, antifungal, antimalarial, antiviral, anti-allergic, anti-dermatic, anti-inflammatory, insecticidal and namaticidal in nature. Powdered neem leaf and neem bark have high surface area. It is also one of the reasons to use neem as adsorbent. Few studies have been performed using neem leaf as an adsorbent (Alau, *et al.*, 2010) [2]. Comparison study of neem leaves, neem bark and neem seed (coat and kernel separately) has not been reported yet. In this study, adsorption capability of adsorbents derived from neem tree was evaluated using methylene blue dye.

Materials and Methods

Preparation of Adsorbents

Four types of adsorbents were prepared from neem (*Azadirachta indica*) parts namely leaf, bark, seed coat and seed kernel by following same procedure. Raw materials were collected from a neem tree. Seed coat and seed kernel were first separated before making the adsorbents from neem seeds. Then collected raw material were washed to remove the impurities and dust particles. They were kept in drying oven for 24 hours at temperature 105℃. Dried materials were powdered eventually. Then the powder were sieved by 0.71mm sieve. They were stored in air tight containers until used.

Preparation of Adsorbate

Methylene blue (MB) dye was used as an adsorbate since it is used for evaluating the adsorbents frequently. One gram of MB dye was dissolved in 1000ml of distill water to prepare stock solution. Four level of working concentrations (50mg/L, 100mg/L, 150mg/L and 200mg/L) were prepared using the stock solution.

Characterization of Adsorbents

Moisture content, organic matter content, ash content, pH, electrical conductivity and bulk density were determined to characterize the adsorbents.

Determination of moisture content

Gravimetric moisture determination method was followed as follows (Dada, 2012) [5].

$$\text{MC}\,\% = \frac{W_2 - W_3}{W_2 - W_1} * 100$$

Where,
W_1 = weight of empty crucible (g)
W_2 = weight of crucible with sample before drying in the oven (g)
W_3 = weight of crucible with sample after drying in the oven (g)

Determination of volatile matter content

Empty crucibles were weighed. Approximately 10g of oven dried at 105°C adsorbents were put into the crucibles and weighed. They were placed in the muffle furnace and heated for one hour and thirty minutes at constant temperature of 760 °C (Dada, 2012) [5]. The samples were then removed and cooled in a desiccator. Then samples were re weighed. Volatile matter content was calculated by following equation (Dada, 2012) [5].

$$\text{VM\%} = \left(\frac{W_2 - W_4}{W_2 - W_1}\right) * 100$$

Where,
W_1 = weight of crucible (g)
W_2 = weight of crucible with sample before drying in muffle furnace (g)
W_4 = weight of crucible with sample after drying in muffle furnace (g)

Determination of ash content

Ash content was calculated by following equation (Dada, 2012) [5].

$$\text{Ash content\%} = \left(\frac{W_4}{W_2 - W_1}\right) * 100$$

Where,
W_1 = weight of empty crucible (g)
W_2 = weight of crucible with sample before heating (g)
W_4 = Final weight of crucible with sample (g)

Measurement of pH

One gram of each adsorbents (seed outer shell, seed kernel, bark and leaf) were dissolved in 100 ml distilled water. Solutions were shaken for few minutes to provide adequate mixing. The pH of each samples were measured using a pH meter (Model-CE470,HACH) and the readings were recorded (Dada, 2012) [5].

Measurement of electrical conductivity

One gram of each adsorbents (seed outer shell, seed kernel, bark and leaf) were dissolved in 100 ml distilled water. Solutions were shaken for few minutes to provide adequate mixing. Then the solutions were properly mixed for few minutes and EC was measured using an electrical conductivity meter (Model-CE470, HACH).

Determination of bulk density

The bulk density of each adsorbents were determined using Archimedes' principle by weighing a 10cm^3 measuring cylinder before and after filling with the samples (Dada, 2012) [5].

$$\text{BD} = \frac{W_2 - W_1}{V}$$

Where,
W_1 = weight of empty measuring cylinder after drying (g)
W_2 = weight of cylinder filled with sample after drying (g)
V = volume of cylinder (ml)

Determination of MB dye concentration after adsorption

Adsorption of MB by adsorbents were determined by measuring the amount of dye present in solution. Measurement of dye (MB) in solution was determined using a calibration curve prepared for methylene blue using the peak absorbance wavelength of 660nm. UV visible spectrophotometer (UV-1240, Japan) was used for the absorbance measurements.

Experimental arrangement
Four types of adsorbents (neem seed coat, seed kernel, bark and leaf) were used for the experiment. Three levels of adsorbents (1g, 2g and 3g) in each type were used. Four levels of adsorbate (50mg/L, 100mg/L, 150mg/L and 200mg/L) were used.

Experimental procedure
Batch experiments were conducted to determine the removal of methylene blue dye by adsorption using four types of adsorbents prepared from neem tree at three different dosage levels. Three replicates were used for each experiment. One hundred milliliter of adsorbate was taken into a 250ml beaker and predetermined amount of adsorbent (1g, 2g and 3g) were added. Then the mixture was shaken in a mechanical shaker (30rpm) for about 50 minutes and allowed for settling. Then solution were filtered by whatman filter paper (no 42) and the dye concentration in solution was determined by measuring the absorption at 660nm. The absorption was taken using a UV visible spectrophotometer (UV-1240, Japan).
The amount of adsorbed dye (mg/g) was calculated using the following equation.

$$Q = \frac{V(C_0 - C_f)}{W}$$

Where,
Q = the amount of dye adsorbed from the solution (mg/g)
V = volume of the adsorbate (ml)
C_0 = dye concentration before adsorption (mg/L)
C_f = dye concentration after adsorption (mg/L)
W = the weight in gram of the adsorbent (g)
The adsorbate removal efficiency was determined by computing the percentage adsorption using the formula,

$$\text{Adsorption } \% = \left(\frac{C_0 - C_f}{C_0}\right) * 100$$

Effect of types of adsorbents
Effect of different adsorbent on adsorption was analyzed.

Effect of initial dye concentration
To find out the effect of initial adsorbate concentration on adsorption, four levels of dye concentrations (50 mg/L, 100mg/L, 150 mg/L, 200 mg/L) were used.

Effect of adsorbent dosage
The effect of adsorbent dosage on adsorption efficiency was studied. Three adsorbent doses were used in each adsorbent (1g, 2g and 3g).

Isotherm
The modelling of adsorption was studied to identify the method of dye adsorption. Freundlich and Langmuir isotherms were tested to determine the adsorption process. For Langmuir isotherm following linearized equation was used.

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max}k_L} + \frac{c_e}{Q_{max}}$$

Where,
Q_e - Amount of methylene blue adsorbed per unit weight of adsorbent (mg/g)
Q_m - Maximum amount of methylene blue adsorbed per unit weight of adsorbent (mg/g)
K- Adsorption equilibrium constant (L/mg)
C_e – Equilibrium concentration of methylene blue (mg/L)

Following equation was used to determine the adsorption process by Freundlich isotherm
Where,

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

q_e- Amount adsorbed at equilibrium (mg/g)
K_f - Freundlich constant
1/ -Heterogeneity factor, related to the capacity and intensity of the adsorption
Ce- Equilibrium concentration (mg/L).

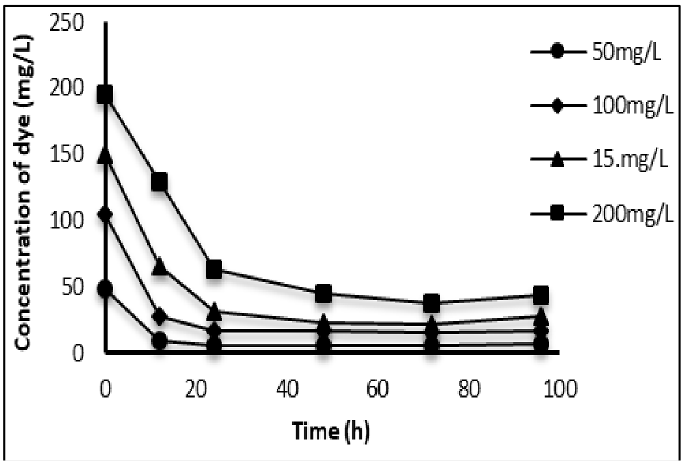
Results and Discussion

Adsorbent characterization
Adsorption process depends on the physiochemical properties of adsorbents.
The high fixed carbon level (>68%), low ash content level (<15%) and high bulk density are main properties that can be used to identify the good adsorbent (Adamson, 1979). All four adsorbents have shown optimum level of MC%, ash % and OM%. Therefore each has the capacity of pollutant removal. Among them, neem seed coat showed low ash content and second high OM%. The values are given in the table 1.

Table 1 : Properties of adsorbents

0	Physiochemical property					
	MC %	**OM %**	**Ash**	**pH**	**EC**	**BD(g/cm^3)**
Leaf	1.4(±0.07)	91.25(±0.73)	8.75(±0.05)	5.66(±0.04)	1040(±4)	0.031(±0.04)
Bark	3.33(±0.05)	95.69(±0.07)	4.31(±0.05)	6.13(±0.03)	303(±3)	0.036(±0.02)
kernel	1.33(±0.01)	96.99(±0.58)	3.01(±0.04)	5.95(±0.04)	653(±10)	0.022(±0.03)
Seed coat	9.5(±0.03)	95.83(±0.30)	4.17(±0.06)	5.67(±0.04)	325(±3)	0.067(±.05)

Color removal by different adsorbents
Concentration of MB dye reduced with the time after the application of adsorbents. Five milliliter of adsorbate was taken at 12hours, 24 hours, 48, hours 72hours and 96hours, filtered and determined the dye removal by adsorption. Dye removal rate was very high during 12 hours for every adsorbents. After that removing rate is decreasing with time. Seed coat showed very high and quick color removal compared with other adsorbents. After 24 hours of settling time, the color removal was approximately equal in all adsorbents (figure 1).



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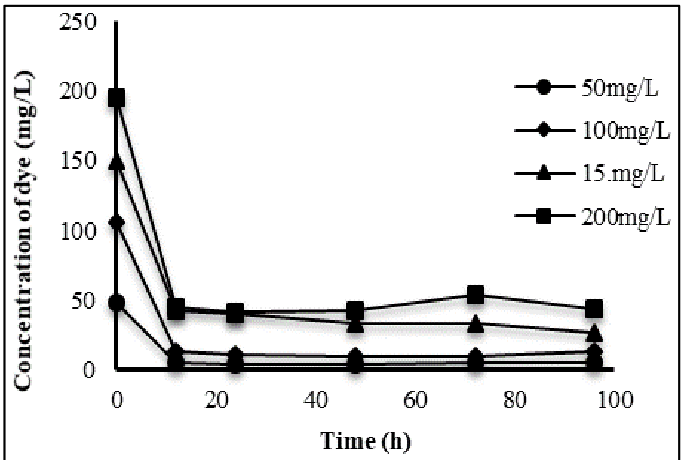

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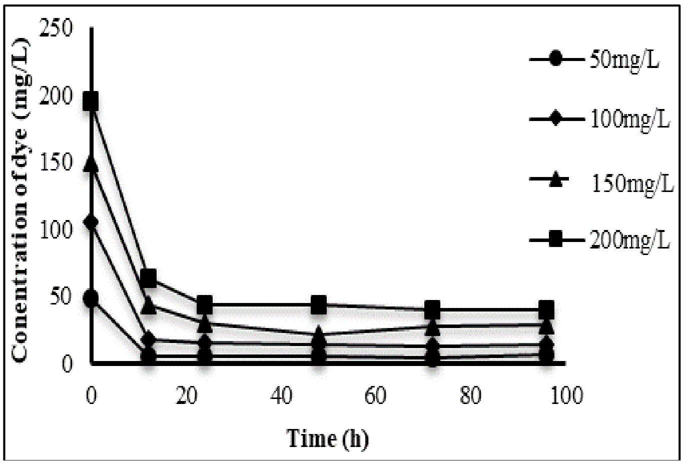

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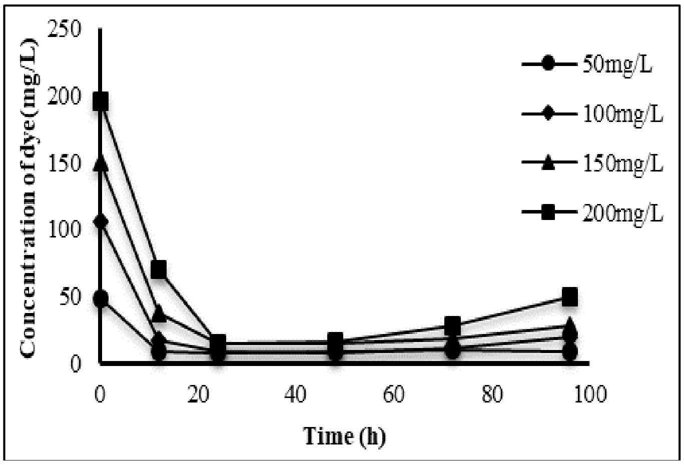
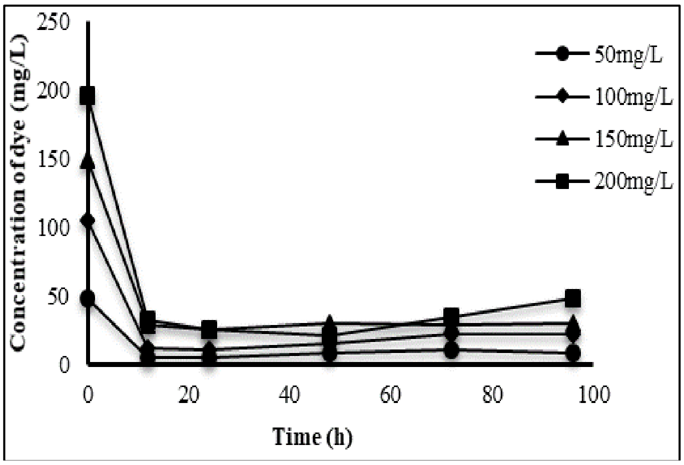


D

Fig 1: Reduction of dye by adsorbent derived from neem leaf with time at different doses of 1g(A), 2g(B) and 3g(C) at pH of 6.



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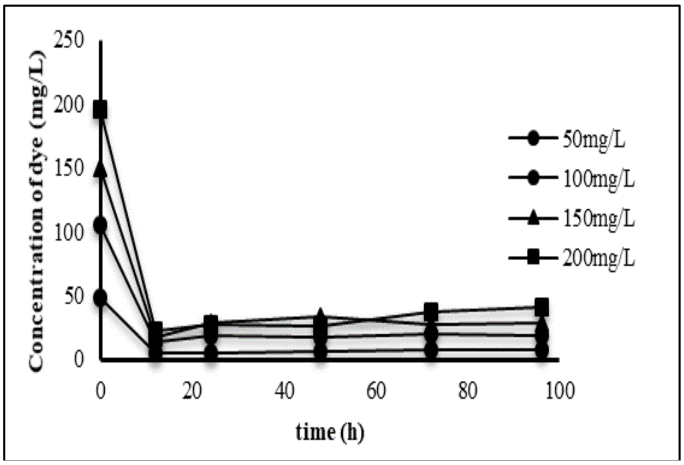

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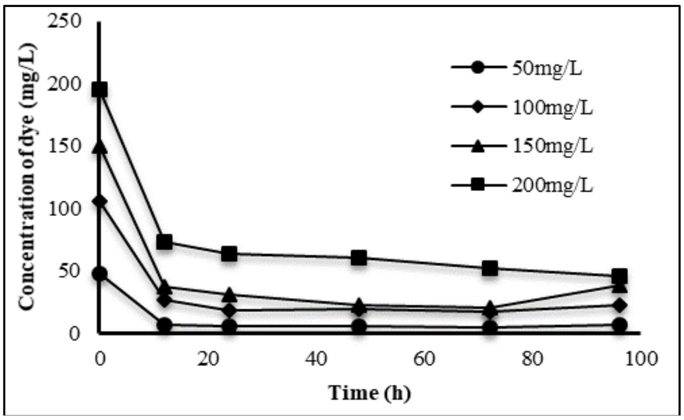
Fig 2: Reduction of dye by adsorbent derived from neem bark with time at different doses of 1g(A), 2g(B) and 3g(C) at pH of 6.



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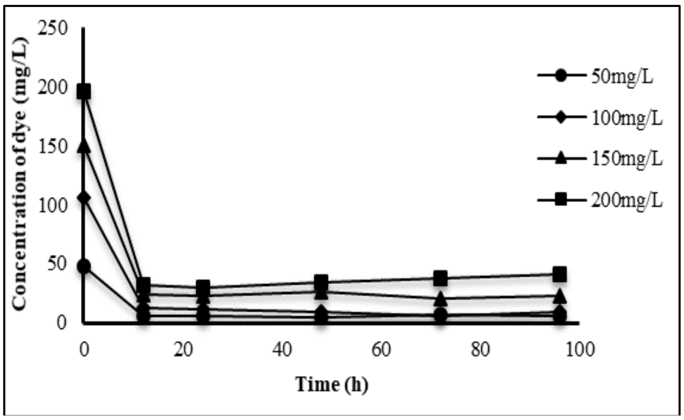

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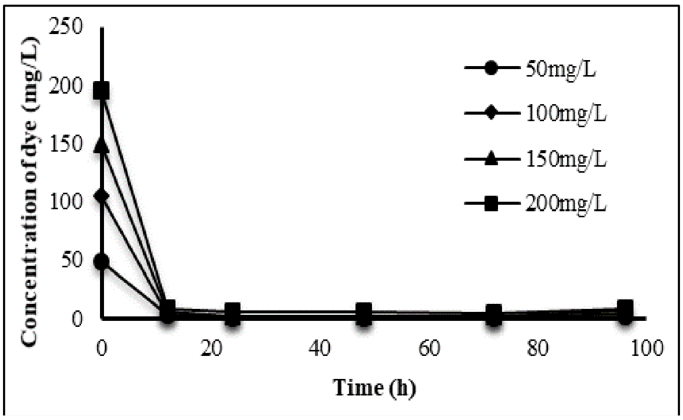
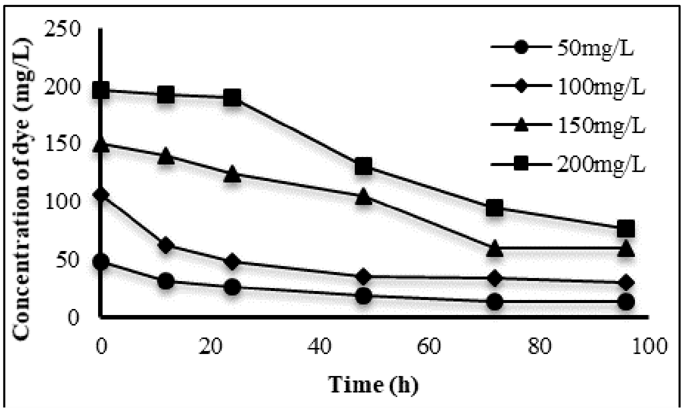


C

Fig 2 : Reduction of dye by adsorbent derived from neem seed coat with time at different doses of 1g(A), 2g(B) and 3g (C) at pH of 6.



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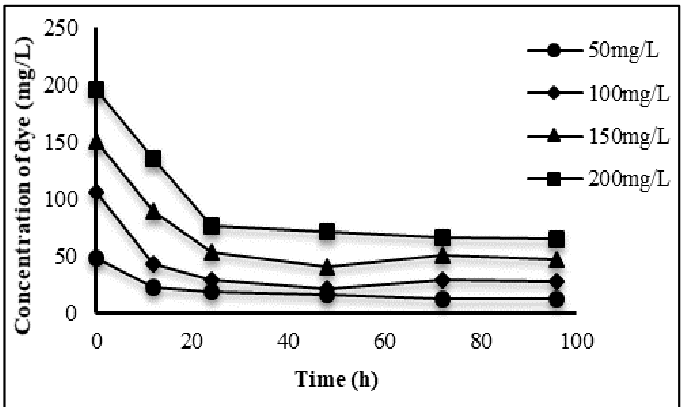

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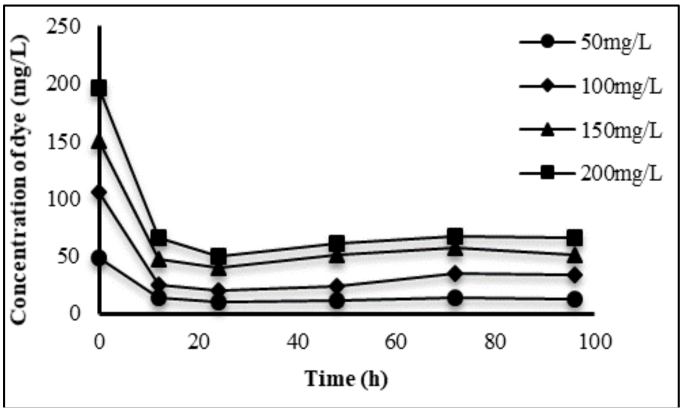

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Fig 3: Reduction of dye by adsorbent derived from neem seed kernel with time at different doses of 1g(A), 2g(B) and 3g(C) at pH of 6.

Adsorption rate
Initial and the final concentration of adsorbate shows the rate of adsorbate removal by the adsorbents. Initial concentration of the known adsorbate was derived by the calibration curve. Each adsorbent showed satisfactory pollutant removal efficiency. They removed dye from the aqueous solution more than 70%. Seed coat showed high adsorption rate. It showed high dye removal capacity more than 87%. Seed kernel showed low dye removal compared with other adsorbents. The amount of adsorbate adsorbed per unit weight (Q) of seed coat is higher than that of other adsorbents due to the high adsorption rate of it. The second highest Q was reported by the leaf adsorbent.

Adsorbent comparison
General Linear model ANOVA was used to determine the adsorption efficiency of each adsorbents with the various adsorbent doses and various initial adsorbate concentration. Average adsorption capacity of each adsorbents of this present study is shown in figure 6. Grouping was done using the fisher LSD method with 95% confidence. There was a different grouping among the adsorbents. It proved that the adsorption of dye was varied with different adsorbents. Seed coat showed high adsorption capability 87% compared with other adsorbents. Study ensured that pollutant removal effect of seed kernel is low among other adsorbents. However it showed 69% of color removing

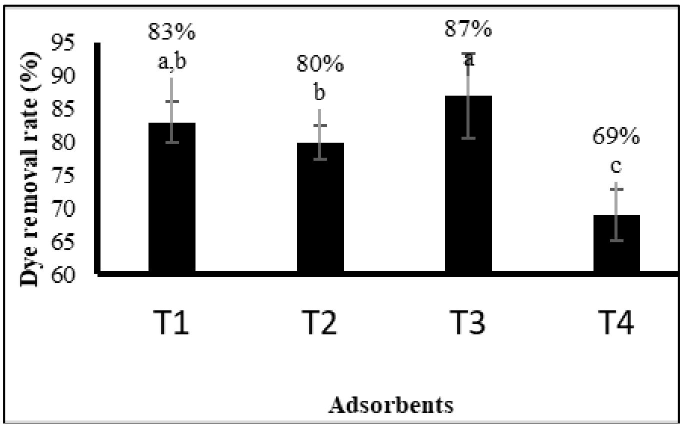
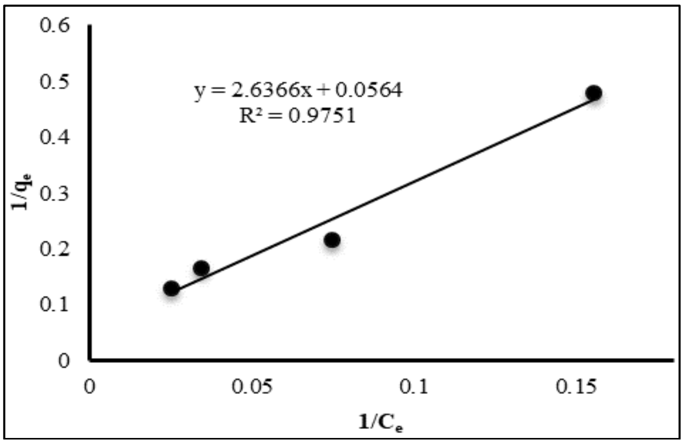


Fig 4: Adsorption rate of adsorbents.

Effect of adsorbent dose on adsorption rate
Adsorption capacity was changed with adsorbent doses. Adsorption rate was high when 3g of dose is used. While the 1g of adsorbent reduces the adsorption. If adsorbent dose increases, adsorption capacity also increases.
Amount of dye adsorbed per unit weight of adsorbent decreases with increases of adsorbent doses. When dose increases, available adsorption sites also increase. Therefore, amount of dye adsorbed per unit weight of adsorbent (Q_e)

Effect of initial concentration of adsorbate on adsorption
Adsorption capacity increases with adsorbate initial concentration. Amount of dye adsorbed per unit weight of adsorbent increases with increases of adsorbate initial concentration

Langmuir isotherm
Adsorption isotherms were drawn to each adsorbent at optimum dose of 2g. Langmuir constant and maximum amount of adsorbate adsorbed per unit weight of adsorbent were derived using the models (figure 6). Langmuir constant (K_L) implies large surface area and pore volume which result in higher adsorption capacity (Vijayakumar, *et al.*, 2012) [29]. Separation factor R_L was calculated. When R_L value fall within 0-1 value adsorption process is favorable. R_L value of each adsorbent falls between 0-1. So, the adsorption process of four adsorbents is favorable for adsorption (Vijayakumar, *et al.*, 2012) [26].
The maximum adsorbate adsorbed and other important parameter related Langmuir isotherm model are given in table 2. It appears that adsorption by leaf, bark and seed kernel follows the Langmuir isotherm model. However, the R_2 of seed coat is week indicating that it does not follow Langmuir isotherm model



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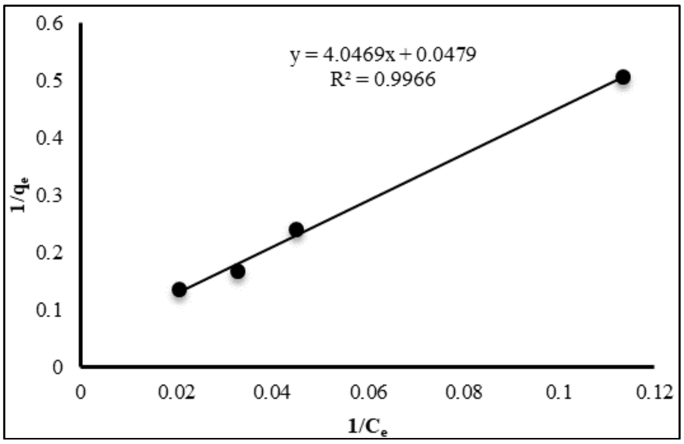

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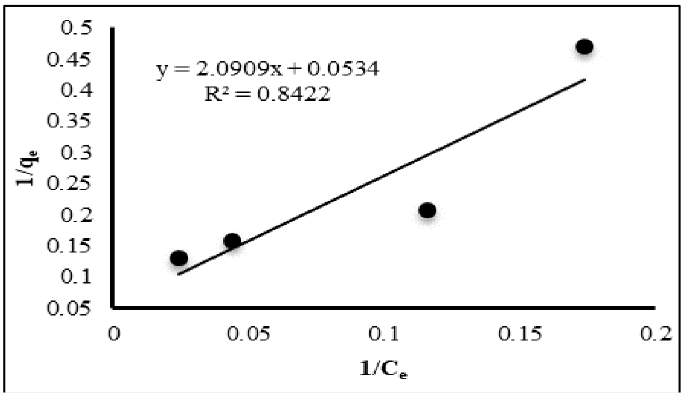

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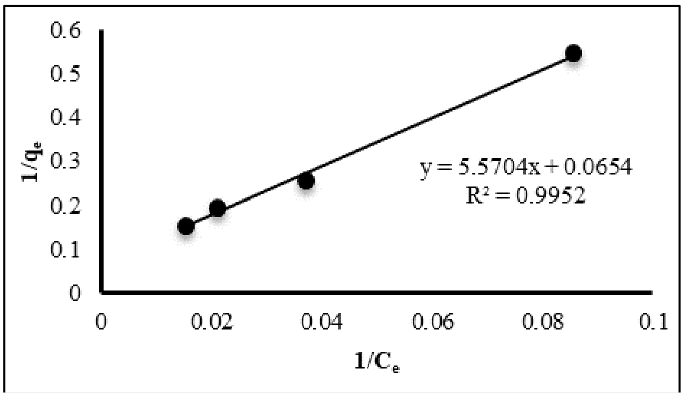


D

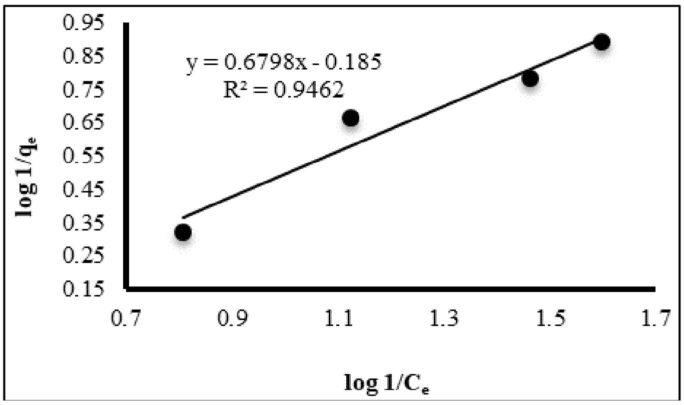
Fig 6: Langmuir isotherm for neem leaf (A), bark (B), seed coat(C) and seed kernel (D)

Table 2: Important parameters related Langmuir isotherm model

Isotherm	K_L	q_{max}(mg/g)	R_L	R^2
Seed coat	0.025539	18.72659	0.270512	0.8422
Leaf	0.021391	17.7305	0.306871	0.9751
Bark	0.011836	20.87683	0.444487	0.9966
Seed kernel	0.011741	15.29052	0.44649	0.9952

Freundlich isotherm

Freundlich isotherm was plot in between log C_e and log q_e of every adsorbent at the optimum dosage 2g. Freundlich constant provide the information about adsorption capacity and 1/n heterogeneity factor indicate adsorption intensity (Vijayakumar, *et al.*, 2012) [26]. Isotherm of bark shows higher coefficient of determination. Heterogenic factor (1/n) is high for seed bark and seed outer code has low value.



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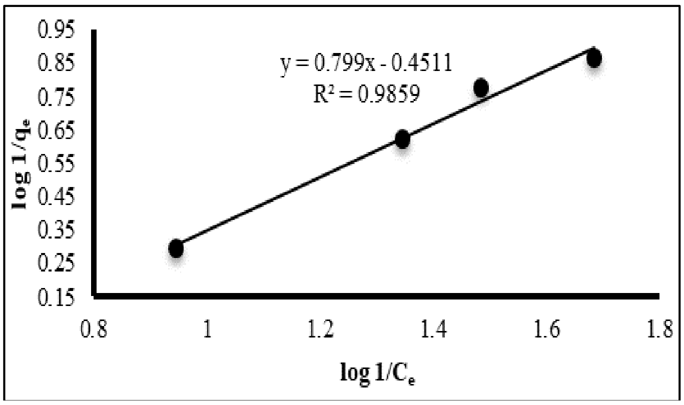

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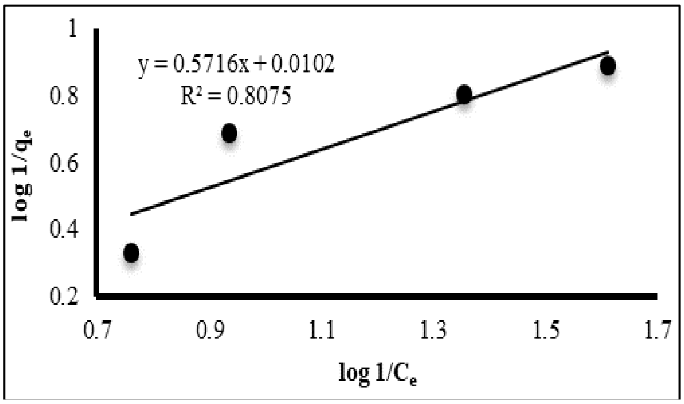

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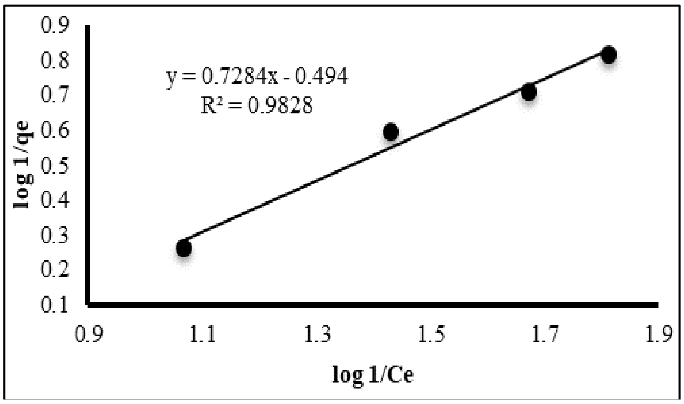

D

Fig 5: Freundlich isotherm for neem leaf (A), bark (B), seed coat(C) and seed kernel (D)

Table 3 : Important parameters related to freundlich isotherm model

Isotherm	K_f	1/n	N	R^2
Seed outer Code	1.1918	0.6367	1.5705	0.8075
Leaf	0.6531	0.6798	1.4710	0.9462
Bark	0.3539	0.799	1.2515	0.9859
Seed kernel	0.3206	0.7284	1.3728	0.9828

Langmuir isotherm provide maximum R^2 or best fit for all adsorbent except seed coat. Therefore, the adsorption involves the attachment of only one layer of molecules to the surface. They all are monolayer adsorption. The surface of adsorbents is uniform, all the adsorbents sites are equivalent. Adsorbed molecules do not interact.

All adsorption occurs through the same mechanism. However R^2 for seed coat for both isotherm models shows low values. It appears that the adsorption by seed coat does not follow these two isotherm models.

Conclusion

Results indicate that each adsorbent has an ability to remove the methylene blue from aqueous solution. Seed coat is the best adsorbent among four other adsorbents. It showed 87% of adsorption efficiency. Adsorbents from the leaf, bark, seed kernel takes next places. They showed 83%, 80% and 69% of adsorption efficiency respectively.

Adsorption rate is decreased with the increases of concentration of adsorbate. Dye removal is increased when adsorbent does is increased

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