Decolourization of Brown Sugar by Adsorption using Activated Charcoal

Rasika Shikare, Prathmesh Kale & Dr. Pradnya K. Ingle
Department of Chemical Engineering, Shivajirao S. Jondhale College of Engineering, Sonarpada, Dombivli (E)

Received Dec. 08, 2017 Accepted Jan. 12, 2018

ABSTRACT *The objective of this project work is to study the adsorption of Molasses from brown sugar using activated carbon. Cheap and eco-friendly adsorbent has been used for removal of molasses from aqueous solution. Liquid phase batch operations are to be carried out to observe the effect of various experimental parameters such as contact time, temperature (30°C, 40°C, 50°C), pH, initial concentration of molasses and adsorbent dose (0.5gm/50ml, 1gm/50ml, 2gm/50ml, 3gm/50ml, 4gm/50ml) and the optimumconditions for these parameters are evaluated. Study on adsorption isotherms is also carried out. Comparisons between granulated and powdered activated carbonis done and best out of the two is determined. The amount of molasses adsorbed per unit mass of activated charcoal was calculated by taking different concentrations of solutions for variousexperimental parameters. This project work can help in designing low cost adsorption columns. Also it can be used to purify brown sugar.*

Keywords:*Activated charcoal, Adsorption, Brown sugar, isotherm, Molasses, Rate kinetics*

1. INTRODUCTION.

Brown sugar is a sucrose sugar product with a distinctive brown color due to the presence of molasses. It is either an unrefined or partially refined soft sugar consisting of sugar crystals with some residual molasses content (natural brown sugar), or it is produced by the addition of molasses to refined white sugar (commercial brown sugar). Natural brown sugar, raw sugar, whole cane sugar all retain small to large amount of molasses from mother liquor.
Commercial brown sugar contains 4.5% (light brown) to 6.5% (dark brown) molasses by volume. The regular commercial brown sugar contains 10% by weight molasses.
Activated carbon also known as Activated charcoal, is a form of carbon processed to have small, low volume pores that increases surface area for Adsorption or chemical reaction.
Due to its high degree of microporosity, just one gram of activated carbon has a surface area in excess of 3,000 m^2 as determined by gas adsorption.
Activated carbon is used in gas purification, decaffeination, gold purification, metal extraction, water purification, medicine, sewage treatment, air filter in gas mask and respirators, filters in compressed air and many other applications.

1.1 Literature review

1.1.1 Origin

Origin of brown sugar

Brown sugar has a long history, being the earliest recorded sugar used. It has been grown all over the world, and reached a popularity peak in the 1700s with the rise of Atlantic sugar plantations. It comes in several types, and while it originally was an unfinished form of refined sugar, now it is more often created by adding molasses to white sugar (for better consistency). It has almost identical food properties to white sugar, but adds a molasses-like flavour to foods.
Sugar cane was first cultivated in southwest Asia, where Marco Polo reported in his famous journals that the Chinese used dark brown sugar freely, but did not refine it further. Sugar cultivation spread to the Middle East and the Mediterranean trade circle in the twelfth and thirteenth centuries. In the fourteenth century, the island of Cyprus in the Mediterranean was the location of major sugar farms, using Syrian and Arab slaves as labour. Sugar cane cultivation was made a science in the fifteenth century in Sicily, with the invention of the roller mill, which speeded up the cane processing and freed up slaves to increase the volume of sugar refined. In those times, brown sugar was a by-product of the sugar refining, and was not used widely in cooking until the sixteenth century.

Origin of activated charcoal

The adsorbent properties of charcoal were described in the 1700s, and the first clinical application occurred in the early 1800s. Early investigators such as Bertrand, Tovery, Hort and Garrod showed the effectiveness of charcoal in the preventing clinical and effects of poisoning in animals and humans.

Over the next 150 years, charcoal was further refined, purified and activated to improve its adsorptive powers. Numerous studies were published clinical benefits of charcoal. Despite this work, charcoal was not widely accepted as an essential tool in the management of poisoned patient until the past 20 years. Over the years the adsorptive properties have been improved manifold.

1.2 Adsorbate

Molasses, or black treacle, is a viscous by-product of refiningsugarcane or sugar beets into sugar. Molasses varies by amount of sugar, method of extraction, and age of plant. Molasses is primarily used for sweetening and flavoring foods. It is a defining component of fine commercial brown sugar.

1.3 Adsorbent

Activated carbon, also called activated charcoal, is a form of carbon processed to have small, low-volume pores that increase the surface area available for adsorption or chemical reactions. Activated is sometimes substituted with active.

Due to its high degree of microporosity, just one gram of activated carbon has a surface area in excess of 3,000 m^2 (32,000 sq. ft.), as determined by gas adsorption. An activation level sufficient for useful application may be attained solely from high surface area; however, further chemical treatment often enhances adsorption properties.Activated carbon is usually derived from charcoal and is sometimes utilized as bio char. Those derived from coal and cokeare referred as activated coal and activated coke respectively. Physically, Activated carbon binds material by van der Waals force.

1.4Adsorption

It is the process of formation of a layer of solid or gas on the substrate. It involves separation of a substance from fluid phase by accumulation on the substrate of solid phase

1.5Mechanism of adsorption

Adsorption is a three step process. At first the adsorbate diffuses from fluid stream to the external surface of adsorbent. Secondly the adsorbate shifts to the pores of the adsorbent particles. Majority of adsorption occurs in these pores because of their large surface area. Finally the molecules adhere to the surface area of pores.

Adsorption is a surface phenomenon which results out of binding forces between atoms, molecules and ions of adsorbate and the surface of adsorbent.

1.6 Adsorption kinetics

In order to investigate the controlling mechanisms of the adsorption processes like mass transfer and chemical reactions, pseudo first-order and pseudo second-order kinetic studies are used to test the experimental data.

The pseudo first-order kinetic model has been given by "Lagergren" (1898) for the adsorption of solid or fluid systems and its formula is given as;

$$\frac{dq}{dt} = k_1 * (q_e - q_t)$$

After integrating we get;

$$\ln(q_e - q_t) = \ln q_e - k_1 * t$$

Where q_t is the adsorption capacity at time't' (mg g^{-1}) and k_1 (min^{-1}) is the rate constant of the pseudo first-order adsorption.

Ho's pseudo second –order kinetic model is based on the assumption that the adsorption follows second order chemisorption. Pseudo second-order kinetic model is given by;

$$\frac{dq}{dt} = k_2 * (q_e - q_t)^2$$

After integration;

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

Where k_2 (g mg^{-1} min^{-1}) is the rate constant of the pseudo second-order adsorption and q_t is the adsorption capacity at time't' (mg g^{-1}).

1.7Adsorption isotherms

Adsorption isotherms help in describing how molecules of adsorbate interact with adsorbent surface. The adsorption processes are generally described by the Langmuir and Freundlich isotherm models.

The Langmuir equation is based on the fact that there is no interaction between the adsorbate molecules and that the adsorption process is localized in a monolayer. It then assumes that once a dye molecule occupies a given site, no more adsorption can take place at the site. The Langmuir equation is commonly expressed in the linear form;

$$\frac{1}{q_e} = \frac{1}{b * q_o * C_e} + \frac{1}{q_o}$$

Where C_e is the equilibrium concentration of brown sugar solution (mg L^{-1}), q_e is the equilibrium capacity of the molasses on the adsorbent (mg g^{-1}), q_o is the monolayer adsorption capacity of the adsorbent and b is the Langmuir adsorption constant(L mg^{-1}) and is related to the free energy adsorption.

The Freundlich adsorption model assumes that adsorption takes place on heterogeneous surfaces. Its linear form can be written as;

$$\ln q_e = \ln k_f + \frac{1}{n} * \ln C_e$$

Where k_f and n (dimensionless constants) are the Freundlich adsorption constants, which indicates the capacity and intensity of the adsorption, respectively.

2. MATERIALS AND METHODS.

2.1 Materials

2.1.1 Adsorbent

Activated charcoal is used as adsorbent for molasses removal.

Bulk density: 34.4 kg/m^3

Pore volume: 2 cm^3

Porosity diameter: 0.0044 *10^{-6} m

Specific pore volume: 1.3652 cm^3 g^{-1}

2.1.2 Adsorbate

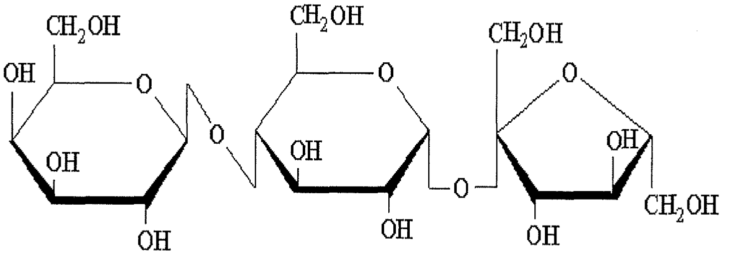


Figure 1: Structure of molasses

2.2 Methods

2.2.1. Plotting calibration curve

Brown sugar solution in water were prepared with concentration 0.04mg/1L, 0.06mg/L, 0.08 mg/L and their % absorbance were found out by UV spectrophotometer (λ_{max}=274). With these values a standard calibration curve was plotted. The equation of the curve was used to calculate the concentrations for various %absorbance.

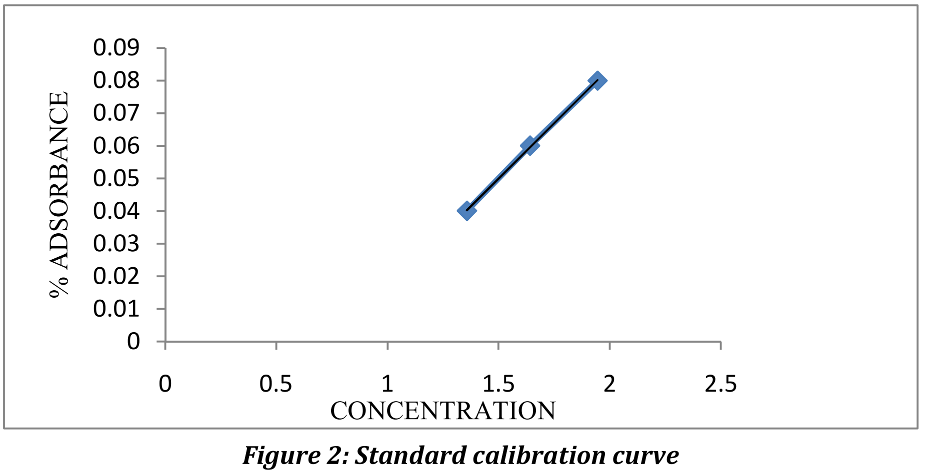


Figure 2: Standard calibration curve

Equation is y=0.068x-0.0521
Now from this equation, concentration can be calculated.
Where x= concentration, y=% absorbance

2.2.2. Effects of various experimental parameters
2.2.2.1. Effect of contact time

500ml of sugar solution with molasses concentration (40mg/L) is to be prepared in a glass beaker with adsorbent concentration (g/L) and kept on magnetic stirrer. The samples were withdrawn at predetermined time intervals % absorbance were estimated by using spectrophotometer to maximum absorbance (λ_{max}=274). The concentrations were measured after 15, 30, 45,60,75,90, 105,120,135 minutes until equilibrium reached. A graph was plotted of $q_t$vs. time. The $q_t$was expressed as;

$$q_t = \frac{(C_0 - C_e)}{M} * V$$

Where, q_t = amount of molasses absorbed per unit mass of adsorbent (mg/g)
C_0= initial concentration (mg/L)
C_e= final concentration (mg/L)

POWDER:

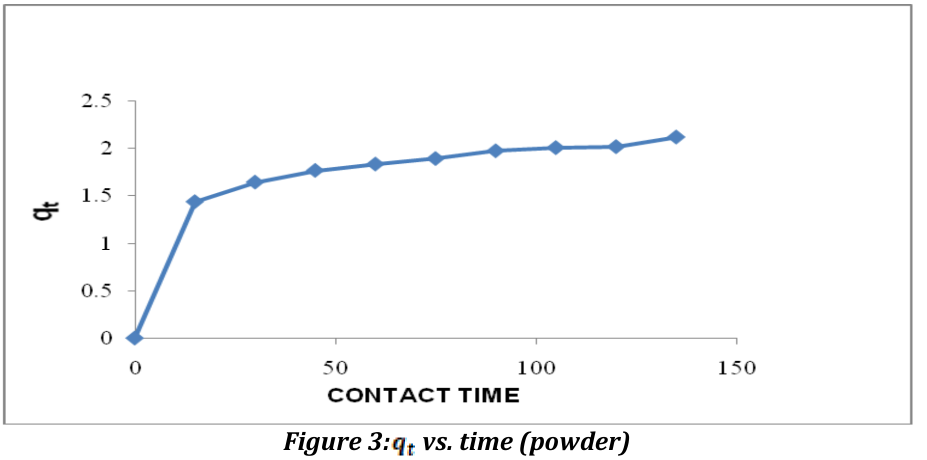


Figure 3: $\boldsymbol{q_t}$ ***vs. time (powder)***

PELLETS:

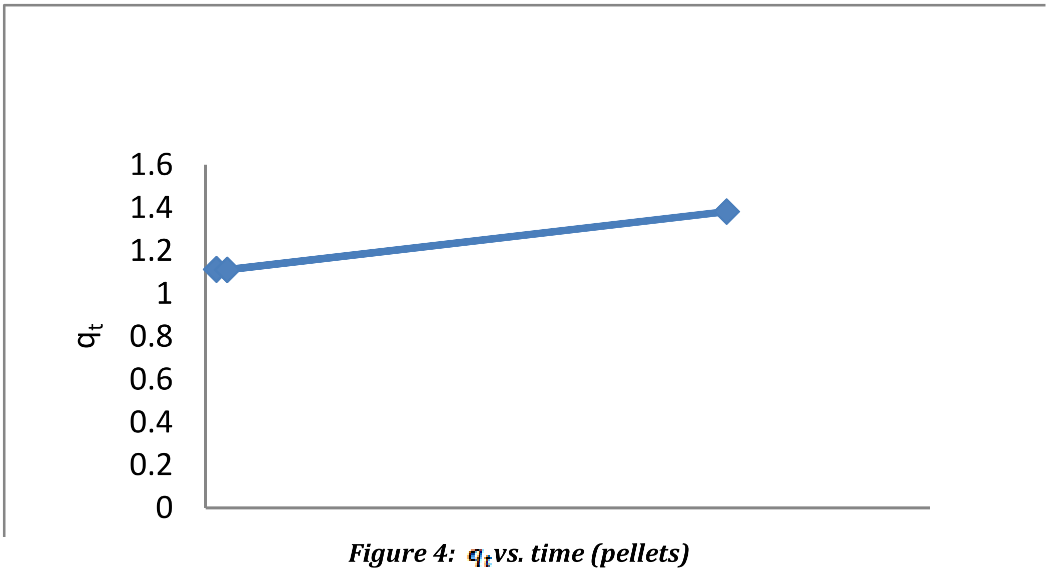


Figure 4: $\boldsymbol{q_t}$***vs. time (pellets)***

2.2.2.2 Effect of temperature
Three solution of brown sugar were prepared (molasses concentration 40mg/L and activated charcoal concentration 1 mg/ml) and were place on magnetic stirrer at different temperatures 30^0 C, 40^0C and 50^0C for 3hrs. Their % absorbance were calculated using spectrophotometer (λ_{max}=274).

POWDER:

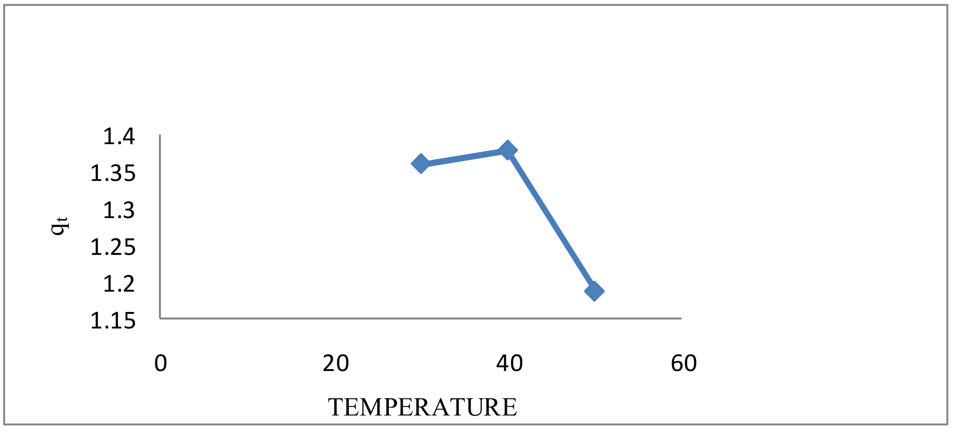


Figure 5: q_t vs. temperature (powder)

PELLETS:

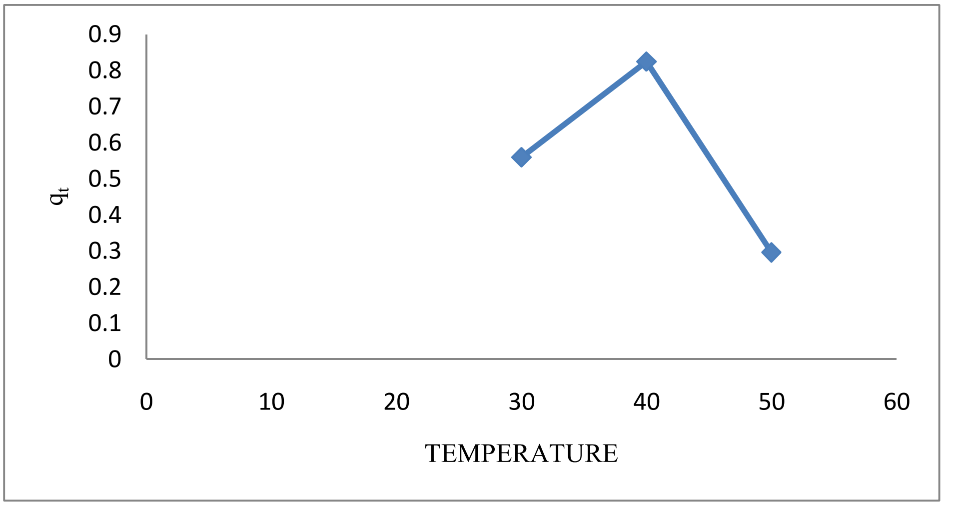


Figure 6: qt vs. temperature (pellets)

2.2.2.3: Effects of initial concentration

POWDER:

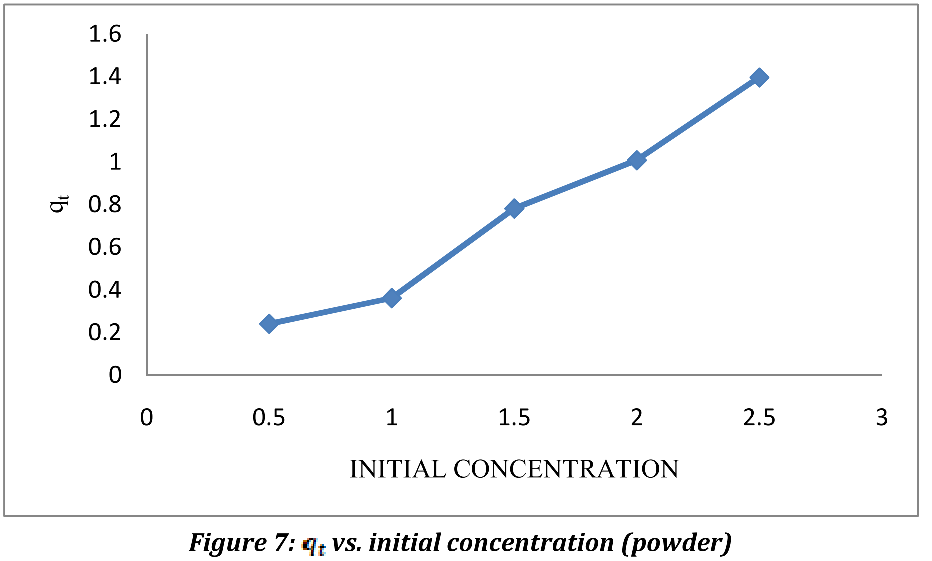


Figure 7: q_t vs. initial concentration (powder)

PELLETS:

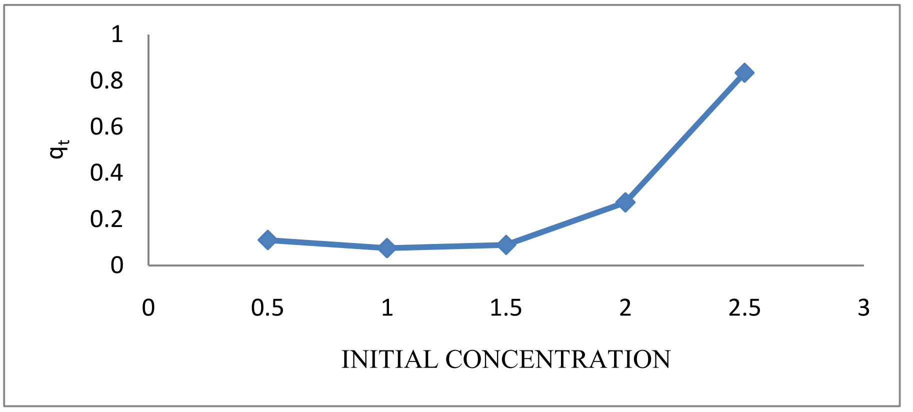


Figure 8 : $q_t$vs. initial concentration (pellets)

2.2.2.4. Effects of adsorbent dose

Adsorbent dose effect was studied by preparing 5 different solutions of activated charcoal and molasses in distilled water in a beaker with constant concentration of brown sugar solution and varying dosage of activated charcoal 0.5gm/50ml,1gm/50ml,2gm/50ml,3gm/50ml,4gm/50ml. These solutions were prepared and kept on magnetic stirrer for 3 hrs. Then their % absorbance were calculated by spectrophotometer (λ_{max}=274). And thus the amount of adsorbed were calculated.

POWDER:

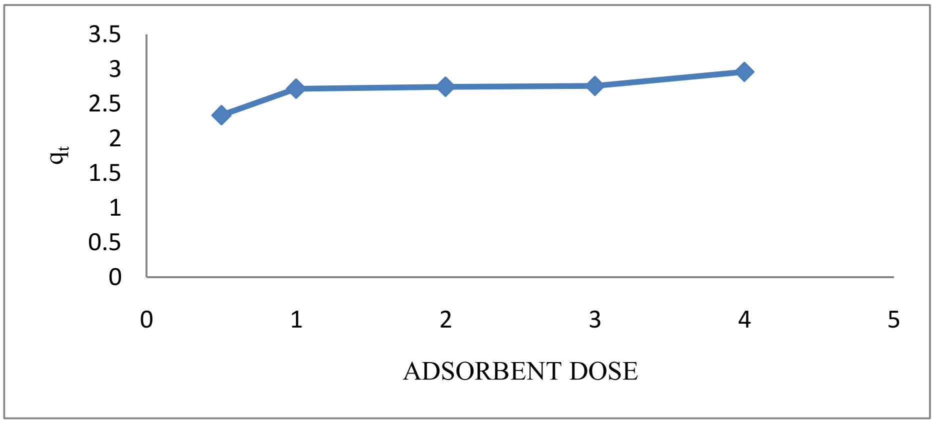


Figure 9: $q_t$vs. adsorbent dose (powder)

PELLETS:

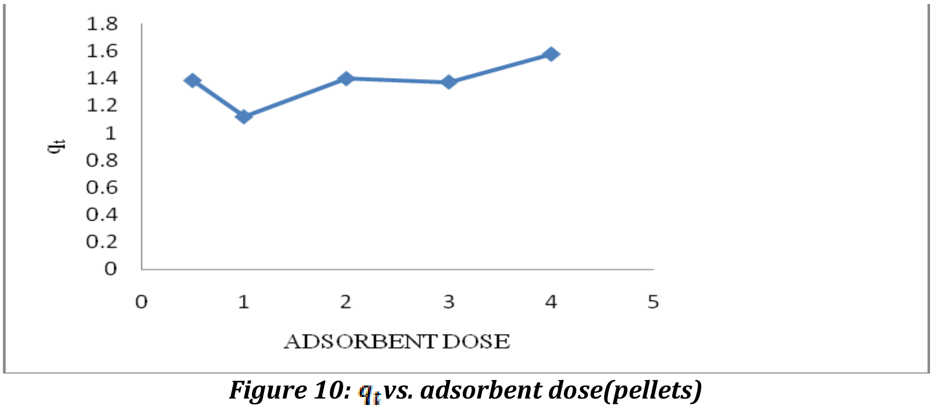


Figure 10: $q_t$vs. adsorbent dose(pellets)

2.2.3. Adsorption kinetics

Brown sugar solution was prepared in a glass beaker with molasses concentration 40mg/L and activated charcoal concentration 5 gm. The beaker were kept on magnetic stirrer (temp=30^{0}c) for 3 hrs. Samples were collected with different time periods and their % absorbance were determined using spectrophotometer (λ_{max}=274). These values were used to calculated q_t (amount of molasses adsorbed per unit amount of activated charcoal) values at different time, the q_t for equilibrium time (180 min) was taken to be q_e. Thus using equations for pseudo first order and second order kinetic model we determine the best fitting kinetic model for the system.

Pseudo first-order kinetic model is given by;

$$\frac{dq}{dt} = k_1 * (q_e - q_t)$$

After integration we get;

$$\ln(q_e - q_t) = \ln q_e - k_1 * t$$

Where q_e and q_t are the amount of molasses adsorbed (mg/g) at equilibrium and at time t respectively. k_1 is the rate constant.

The curves are plotted for pseudo first- order.

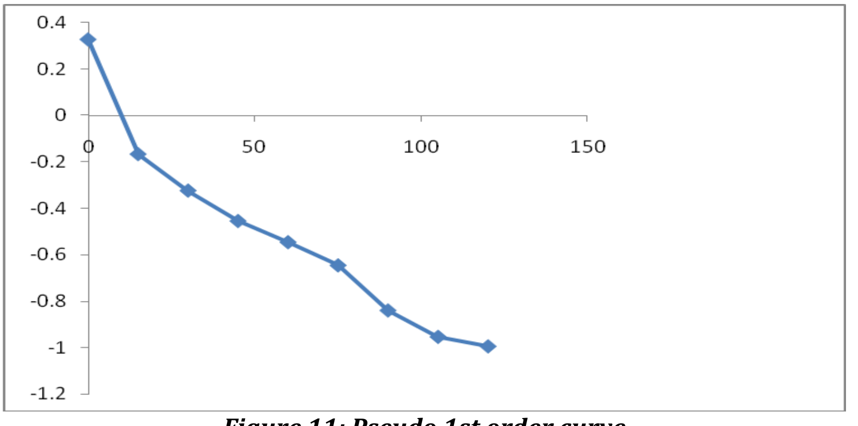


Figure 11: Pseudo 1st order curve

Slope gives k_1 and intercept gives q_e

Table 1: Experimental parameters of pseudo first order

Co	q_{exp}	q_{cal}	k_1	R^2
40	2.12	1.203	-0.0098	0.9259

Pseudo second order kinetic model is given by;

$$\frac{dq}{dt} = k_2 * (q_e - q_t)^2$$

After integration;

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

Where q_e and q_t are the amounts of molasses adsorbed (mg/g) at equilibrium and at time t respectively, k_2 is the rate constant.

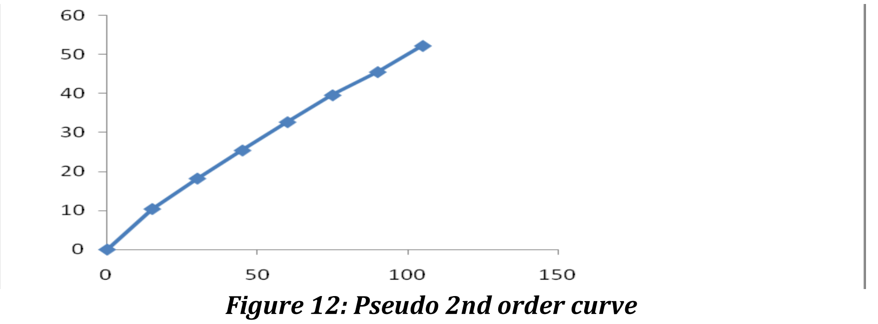


Figure 12: Pseudo 2nd order curve

Slope gives q_e and intercept gives k_2.

Table 2: Experimental parameters of pseudo second order

Co	q_{exp}	q_{cal}	k_1	R^2
40	2.12	2.14	1.40	0.9945

2.2.4. Adsorption isotherms

Temperature	C_e	q_e	lnC_e	lnq_e	C_e/q_e	C_e
30	13.46374	1.252323	2.6	0.225	10.75101	13.46374
40	15.25641	1.349859	2.725	0.3	11.30223	15.25641
50	16.86094	1.440514	2.825	0.365	11.70481	16.86094

Langmuir isotherm model;

$$\frac{C_e}{q_e} = \frac{1}{b * q_o} + \frac{C_e}{q_o}$$

A curve C_e/q_evs.C_e is plotted, the slope gives the q_o value and intercept gives b value

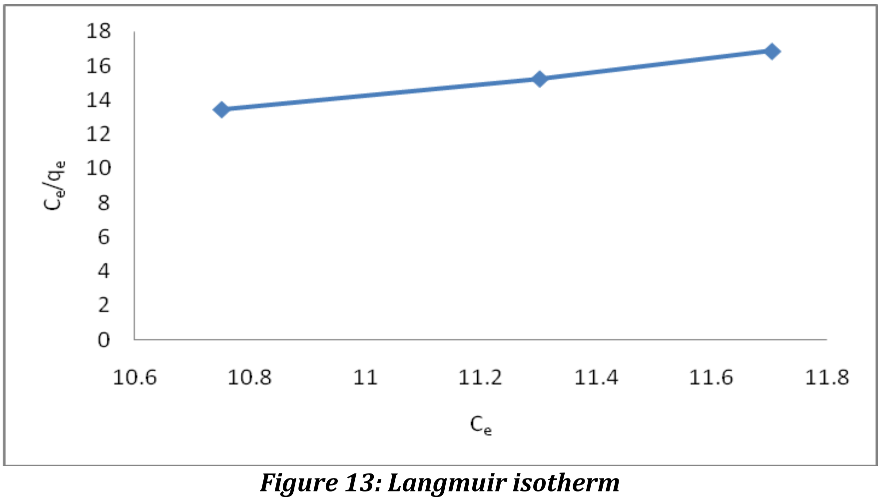


Figure 13: Langmuir isotherm

Freundlich isotherm model;

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e$$

A curve $\ln q_e$vs. $\ln C_e$is plotted, the slope gives 'n' value and interceptgivesk_f value.

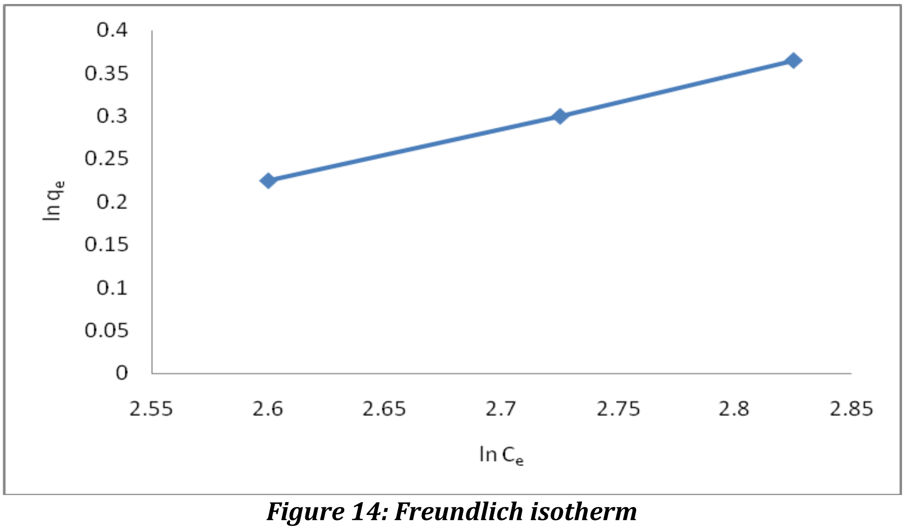


Figure 14: Freundlich isotherm

3. RESULTS AND DISCUSSION.

3.1 Calibration plot

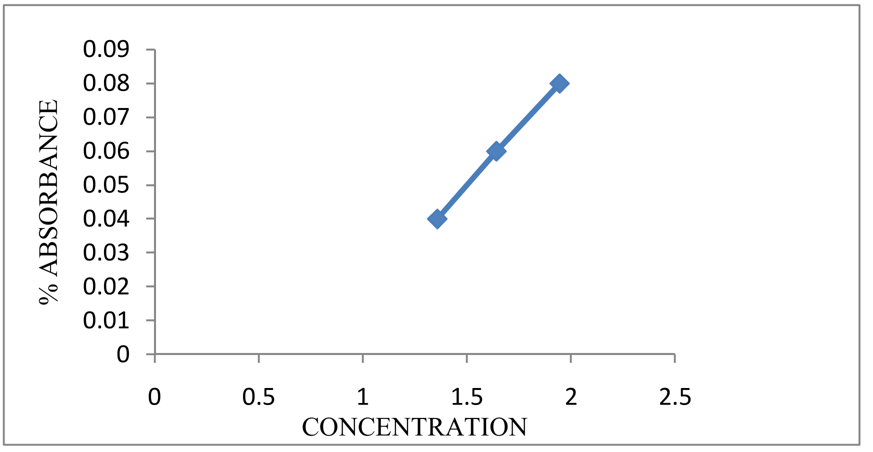
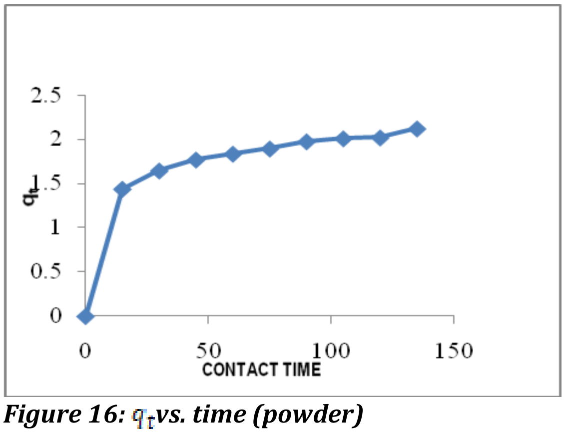


Figure 15: Standard calibration curve

The above plot indicates that the % adsorbance of molasses on activated charcoal increases with increase in concentration of brown sugar solution.

3.2. Adsorption studies

3.2.1. Effect of contact time



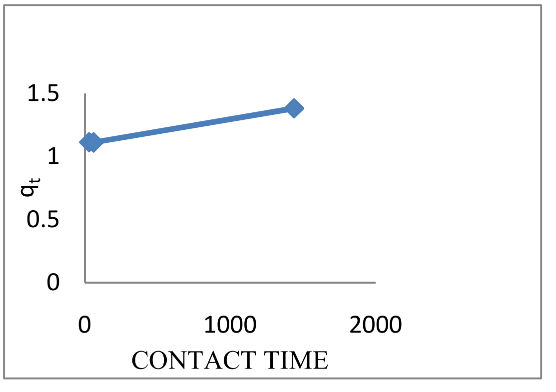
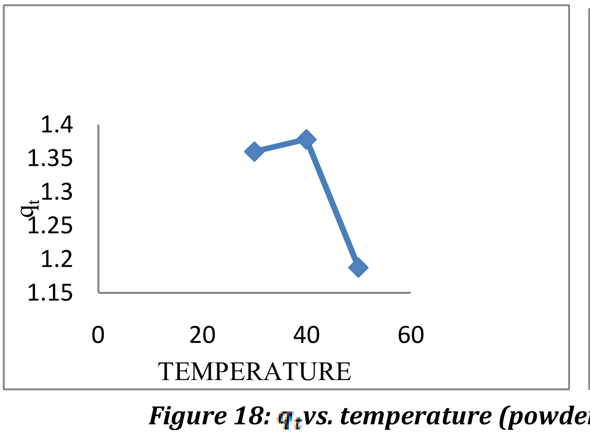


Figure 16: $q_t$vs. time (powder) ***Figure 17: $q_t$vs. time (pellets)***

In case of powdered form of adsorbent, the amount of molasses adsorbed per unit mass of adsorbent first increases gradually and after some tome increases relatively slowly.

In case of pelleted form of adsorbent, the contact time required is more for slight increase in amount of molasses adsorbed per unit mass of adsorbent.

Thus, by using powdered form of activated charcoal, we can get higher amount of adsorbed molasses in lesser contact time.3.2.2. Effect of temperature



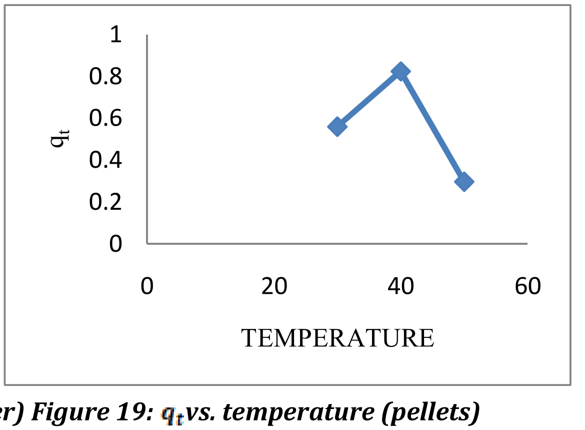
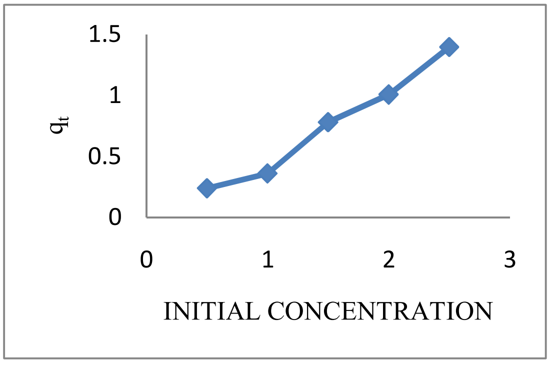


Figure 18: $q_t$vs. temperature (powder) Figure 19: $q_t$vs. temperature (pellets)

In both cases (powdered and pelleted), the amount of molasses adsorbed first increases and then decreases with increase in temperature.
But as we can see, at around 30 degree Celsius temperature, there is a higher amount of molasses adsorbed on powdered form activated charcoal than in pelleted form. Also, the decrease in q_t value with temperature is less in case of powdered form than in pelleted form of activated charcoal.

3.2.3. Effect of initial concentration



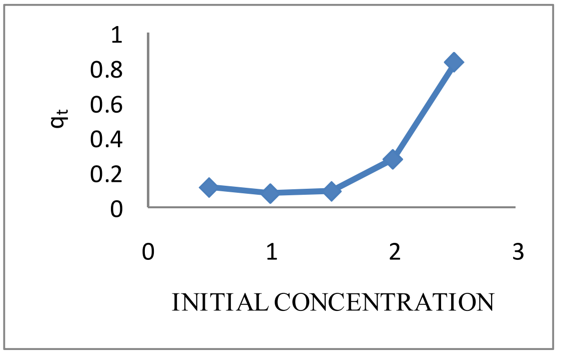
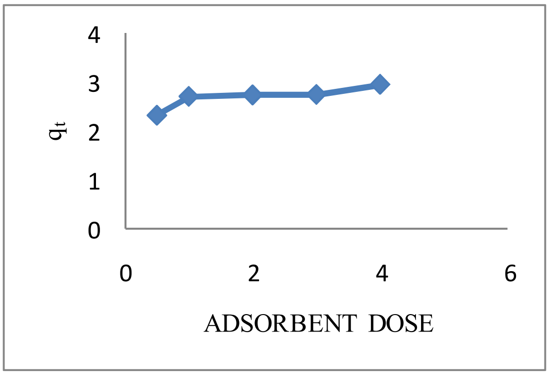


Figure 20: q_t vs. initial concentration (powder) *Figure 21: q_t vs. initial concentration (pellets)*

By using powdered form of activated charcoal, the amount of molasses adsorbed increase with increase in the initial concentration of sugar solution. But if we are using pelleted form of our adsorbent, molasses adsorbed first remains constant and then increases suddenly.

3.2.4. Effects of adsorbent dosage



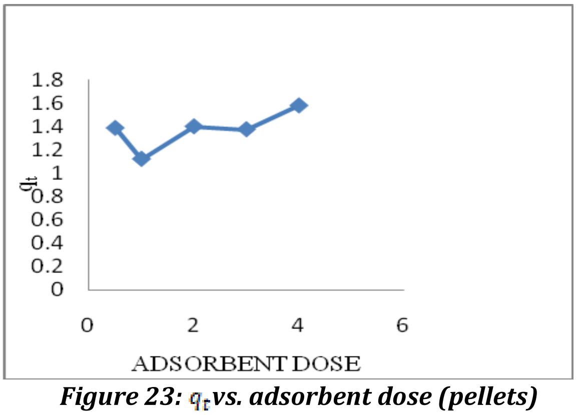


Figure 22: q_t vs. adsorbent dose (powder) *Figure 23: q_t vs. adsorbent dose (pellets)*

If we are using powdered form of activated charcoal, the amount of molasses adsorbed increases slowly. But in case of pelleted form of activated charcoal, it first decreases and then increases slowly. Also the amount adsorbed for powdered form of adsorbent have higher values than pelleted form for same amount of adsorbent dose.

3.3 Adsorption kinetics

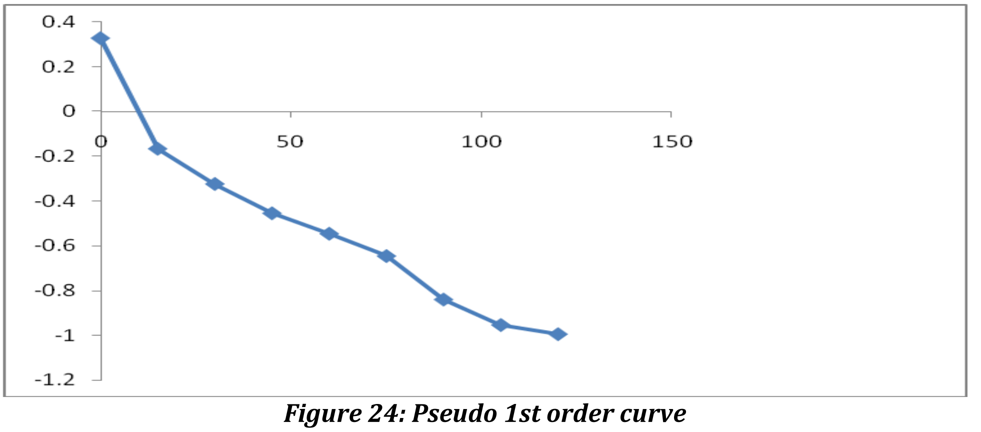


Figure 24: Pseudo 1st order curve

Table 11: Experimental parameters of pseudo first order

Co	q_{exp}	q_{cal}	k_1	R^2
40	2.12	1.203	-0.0098	0.9259

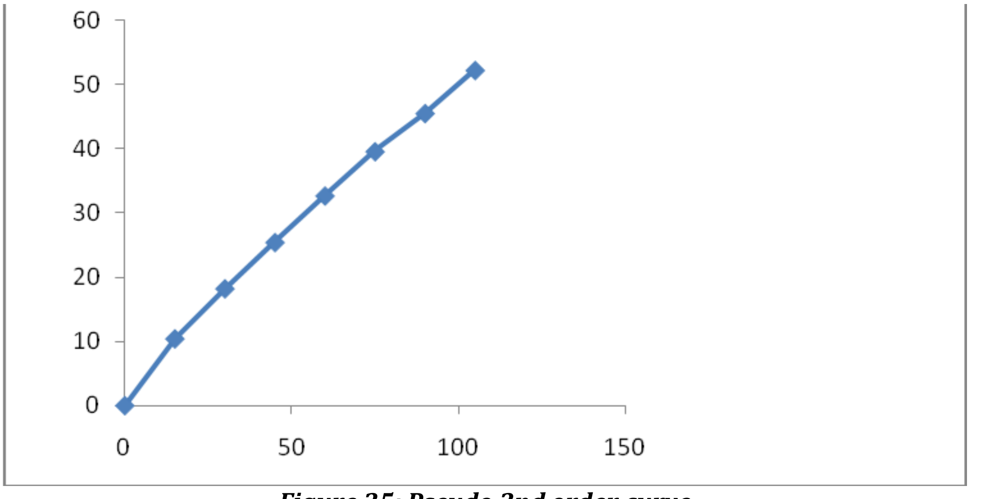


Figure 25: Pseudo 2nd order curve

Table 12: Experimental parameters of pseudo second order

Co	q_{exp}	q_{cal}	k_1	R^2
40	2.12	2.14	1.40	0.9945

3.4 Adsorption isotherm models

Langmuir isotherm curve;

$$\frac{C_e}{q_e} = \frac{1}{b * q_0} + \frac{C_e}{q_0}$$

A curve C_e/q_e vs. C_e is plotted, the slope gives the q_o value and intercept gives b value

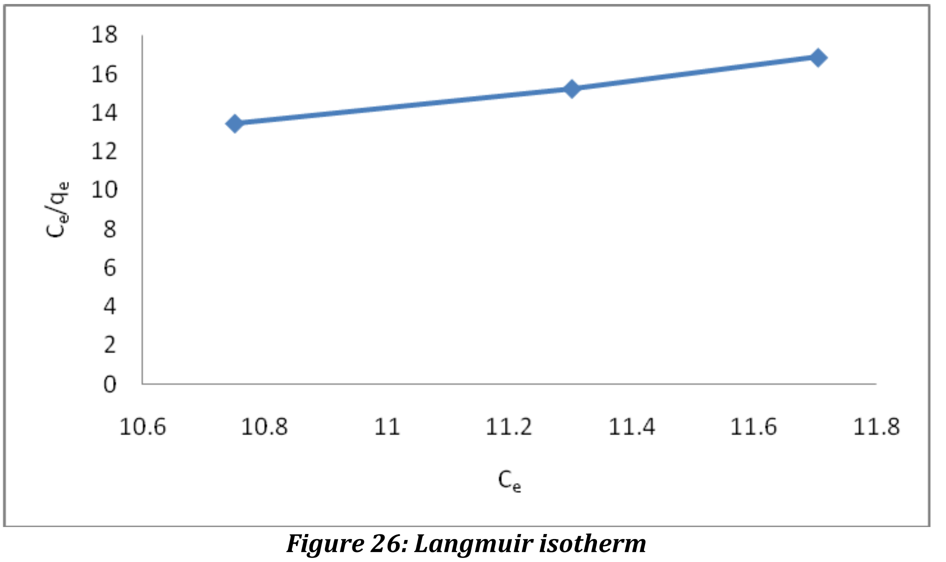


Figure 26: Langmuir isotherm

q_0	B	R^2
0.2822227867	-0.143581327	0.9967

Freundlich isotherm curve;

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e$$

A curve $\ln q_e$ vs. $\ln C_e$ is plotted, the slope gives ‘n’ value and intercept gives k_f value.

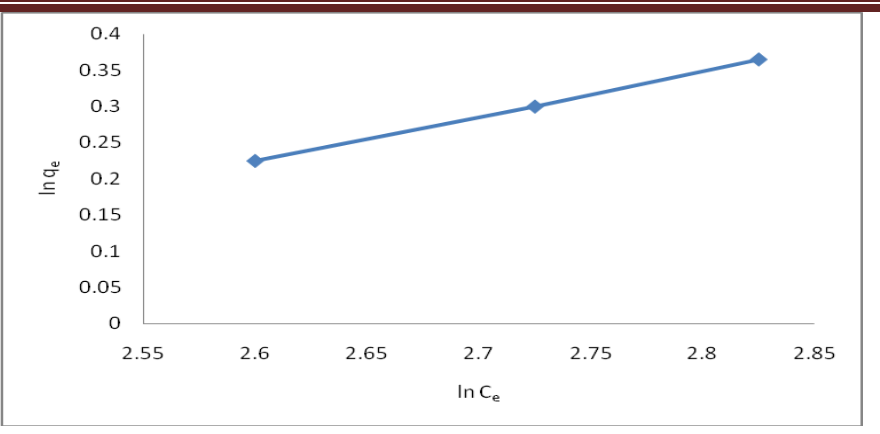


Figure 27: Freundlich isotherm

k_f	n	R^2
0.248776594	1.606528408	0.9995

4. CONCLUSION.

Adsorption of molasses from brown sugar was successfully carried out with the help of activated charcoal (activated carbon). This was effectively used for the decolourization of brown sugar. Various parameters and effects on the adsorption process were studied and their results were displayed in the graphical form. Two forms of adsorbents were used: powdered and pelleted. On comparison, we observed that the use of powdered adsorbent gave better results, in the form of amount of molasses adsorbed per unit mass of adsorbent, than the pelleted form. This adsorption process using activated charcoal will help us to build low cost adsorption columns as the adsorbent is cheap and very effective.

REFERENCES.

[1] Treybal R.E.,*Mass transfer operation, 3 Ed.*, (McGraw Hill New York, 1980).
[2] McCabe W.L. and Smith J.C., *Unit operation in chemical engineering, 5 Ed.*, (McGraw Hill, New York,1993. University of Mumbai B. E. (Chemical Engineering) Rev 2016 Page 60).
[3] Geankoplis C.J., *Transport processes and unit operations*, (Prentice Hall, New Delhi 1997).
[4] J.M. Richardson J.F., Backhurst J.R. and Harker J.H., *Coulson and Richardson chemical Engineering, vol 1 & 2*, (Butterworth Heinman, New Delhi, 2000).
[5] Dutta B.K., *Mass Transfer and separation processes*, (Eastern economy edition, PHI learning private ltd, New Delhi, 2009).
[6] LevenspielO.*Chemical Reaction Engineering*, (John Wiley&Sons, 3ed., 1999).
[7] Smith J.M., *Chemical Reaction Engineering, 3ed*, (TataMcGrawHill,1980).
[8] Fogler, *H.S. Elements of Chemical Reaction Engineering, 4ed.*,(PHI, 2008 University of Mumbai B. E. (Chemical Engineering) Rev 2016 Page 66)
[9] Hill C.G*., Chemical Reaction Engineering*. (5. Walas, Reaction Kinetics for Chemical Engineers, McGraw Hill, 1959).
[10] Walas*, Reaction Kinetics for Chemical Engineers*, (McGraw Hill, 1959).
[11] Himmelblau, D. M. and Riggs, J. B., *Basic Principles and Calculations in Chemical Engineering, 7th edition*, (Prentice Hall of India Pvt. Ltd., New Delhi (2009)).
[12] *Stoichiometry and Process calculations* by K.V. Narayanan and B. Lakshmikutty, (PHI learning Pvt. Ltd).
[13] *Perry's Handbook for chemical Engineers*, Robert H. Perry & Don W. Green, (8th edition, McGraw Hill).
[14] *Instrumental Methods of Chemical Analysis* - S.M. Khopkar.
[15] *Introduction to Spectroscopy* – Pavia, lampman, Kritz.
[16] *Physical chemistry*- Atkins
[17] *Instrumental methods of chemical analysis*-Chatwal-Anand
[18] *Chemical engineering thermodynamics*- B.F Dodge
[19] *Chemical engineering thermodynamics*- Y.V.C Rao
[20] Gregg S.J., and K.S.W. Sing: "Adsorption, surface area, and porosity", Academic New York, 1967.
[21] Hassler, J.W.: "Purification with Activated Carbon", Chemical Publishing, New York, 1962.
[22] Lee, M.N.Y.: in N.N.Li (ed.), "Recent Developments in Seperation Sciences," vol. 1, p.75, Chemical Publishing, Cleveland, 1972.
[23] Ponic, V., Z.Knor, and S. Cerny, "Adsorption on solids," trans by D.Smith and N.G. Adams, Butterwoth, London, 1974
[24] Kinetics of adsorption on carbon from solution-Journal of the Sanitary Engineering Division,1963, Vol. 89, Issue 2, Pg. 31-60.
[25] A Useful Adsorption Isotherm- O. Redlich and D.L Peterson –Journal of Physical Chemistry.Vol.63: Issue 6: Pages. 1024.