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Adsorptive Removal of Methylene Blue from Aqueous Solution Using Agricultural Waste: Equilibrium, Kinetic and Thermodynamic Studies

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Abstract

The potential of raw corn cobs (RCC) powder, for the removal of methylene blue (MB) dye from aqueous solution was investigated. The adsorbent was characterized by FTIR and SEM analysis. Batch adsorption studies were conducted and various parameters such as contact time, adsorbent dosage, initial dye concentration, pH and temperature were studied to observe their effects in the dye adsorption process. The optimum conditions for the adsorption of MB onto the adsorbent (RCC) was found to be: contact time (30mins), pH (10.0) and temperature (343K) for an initial MB dye concentration of 100mg/l and adsorbent dose 1.0g. The experimental equilibrium adsorption data fitted best and well to the Freundlich and Halsey isotherm models. The maximum adsorption capacity was found to be 18.28mg/g. The kinetic data conformed to the pseudo-second-order kinetic model, suggesting that the rate limiting step may be chemisorptions. Adsorption mechanism was investigated with intra-particle diffusion model and it indicated that intra-particle diffusion was not the rate determining step. Thermodynamic quantities such as Gibbs free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) were evaluated. The negative values of ΔG^0 and the positive value of ΔH^0 obtained indicated the spontaneous and endothermic nature of the adsorption process while the positive ΔS^0 value obtained indicated increased randomness during the adsorption process.

Keywords

Adsorption, Methylene Blue, Corn Cobs Powder, Kinetics, Thermodynamics

1. Introduction

Water is an important, rare and precious commodity though it appears to be in plentiful supply on the earth's surface. The ever increasing growth of the world's population and industries have given rise to a constantly growing demand for water in proportion to the supply available which remains constant [1].

The pollution of water resources due to the disposal of dye based effluents has been an increasing worldwide concern for the last few decades. Dyes are natural or synthetic coloured organic compounds having the property of imparting their colours to other substances. Although there are many natural dyes available, the ingrain coloured by these are neither bright nor durable. Hence synthetic dyes are generally used which are cheap and readily available. They also produce brighter colours and are resistant to light, heat and biological degradation [2]. There are more than 10,000 commercially available dyes with over 7×10^5 tonnes of dyestuff being produced annually across the world today [3]. Synthetic dyes are widely used in textile, plastics, cosmetics, pigment, paints, printing, food, pharmaceuticals, paper, tanning and leather industries to colour their products which generate large volumes of coloured wastewater annually [4, 5]. It is estimated that 10 – 15% of the dye is lost during the dyeing process and discharged with the effluent [6].

Methylene Blue (MB) a basic dye is the most common among all other type of its category and it is extensively used in dyeing textile, mostly cotton and silk. It is also used in some medical treatments [7]. However, MB can cause harmful effects such as eye injury to both human and animals. It can give rise to short periods of rapid or difficult breathing on inhalation, while it produces a burning sensation and may cause nausea, vomiting, profuse sweating, diarrhea, gastritis, mental confusion and methemoglobinemia on ingestion through the mouth [8, 9]. Acute exposure to MB can also cause cyanosis, Heinz body formation, Jaundice, quadriplegia and tissue necrosis in humans [10]. Therefore the removal of MB from effluents is essential to protect human, animals and water resources.

Various technologies together with the advantages and disadvantages applied for the treatment of dye effluents were extensively reviewed [11]. Biosorption technology i.e. the adsorption of pollutants by inactive, non-living biomass has been strongly recommended by researchers worldwide as an efficient and economically sustainable technology for the removal of synthetic dyes from industrial effluents [12]. The use of agricultural solid waste (due to its wide spread availability and low cost) for the treatment of dye effluents is not only essential to the environment in clearing the solid waste disposal problems to farmers and agro industries but also to the economy. Some of the agricultural solid waste investigated for the removal of dyes from aqueous solutions include: Guava (Psidiumguajava) leaf powder whose adsorption capacity of Methylene blue was found to be 185.2mg/g [13], Broad bean peel whose adsorption capacity of MB was found to be 192.7mg/g [14], Citrulluslunatus rind whose adsorption capacity of Crystal violet was found to be 11.9mg/g [15], Orange peel whose adsorption capacity of Acid violet was found to be 19.88mg/g [16], Banana peel whose adsorption capacity of Basic Blue 9 was found to be 20.8mg/g [17], Coir pith whose adsorption capacity of Congo red was found to be 2.6mg/g [18] etc.

Nigeria is the largest producers of corn (maize) in Africa and its cobs are left in the environment during processing and after consumption. The availability of corn cobs as waste material is vast in Nigeria. The objective of this study was to investigate the potential of raw corn cob (RCC) powder as an alternative adsorbent for the removal of MB from aqueous solution. Characterizations of RCC powder were done by SEM and FTIR analysis. The effect of contact time, adsorbent dose, initial dye concentration, pH and temperature were evaluated. Adsorption isotherms, kinetics, mechanism and thermodynamic parameters were also evaluated and reported.

2. Materials and Methods

2.1. Adsorbent Collection and Preparation

The raw corn cobs were collected from corn fields of FUTO, Imo state, Nigeria. This agricultural waste was washed thoroughly with water to remove sand, dirt and other impurities present in it and sundried until all moistures were removed. It was then ground in a mill and sieved in a sieve shaker of particle size 80µm. The raw corn cob (RCC) powder that passed through the sieve were stored in an air tight container and used as adsorbent without any further pretreatment.

2.2. Preparation of Adsorbate Solutions

Analytical grade MB dye (C.1.N: 52015, molecular formular: $C_{16}H_{18}N_3SCl$, molecular weight: 319.85, λmax = 664nm) was obtained from a laboratory. A stock solution of MB dye of concentration 1000mg/l was prepared by dissolving 1g of powder MB dye in 1L of distilled water. Experimental dye solutions of desired concentration were obtained by appropriate dilution of the stock solution.

2.3. Adsorbent Characterization

Fourier transform infra-red (FTIR) spectrophotometer was used to identify the different functional groups available on the adsorbent sites and their effect on dye adsorption. The FTIR of the adsorbent was taken before adsorption using FTIR spectrophotometer (Shimadzu-8400S). 0.1g of the adsorbent was encapsulated with 1g of KBr spectroscopy grade (merk, Darmstadt, Germany) and by introducing the mix in a piston's cell of a hydraulic pump with compression pressure $15KPa/cm^2$, the solid transluscent disk was obtained which was introduced in an oven for 4hrs at 105^0C to ensure the non interference of any existing water vapour or CO_2 molecules. The FTIR spectrum was then recorded within the wave number range 4000 –$500cm^{-1}$. In addition, surface morphology and texture of the adsorbent was analyzed using scanning electron microscope (SEM) (Model-PHENOM ProX). Prior to scanning, some quantity of the adsorbent was placed on a double adhesive sticker placed in a sputter machine for 5sec; this gave the adsorbent a conductive property. Sample (adsorbent) stud was fixed on a charge reduction sample holder, and then was charged in the SEM machine.

2.4. Batch Adsorption Experiments

Batch adsorption of MB dye onto the adsorbent (RCC) was conducted in a 250ml airtight Erlenmeyer flask containing 100ml of known concentration of the MB dye solution and an accurately weighed amount of the adsorbent. The mixtures in the flasks were agitated on a mechanical shaker operating at a constant speed of 150 rpm. The effect of contact time (15, 30, 45, 60, 90 &120min), adsorbent dosage (0.5, 1, 1.5, 2 & 3 g/L), initial MB dye concentration (40, 80, 100, 120 &140mg/l), pH (2, 4, 6, 8, 10 & 12) and temperature (303, 313, 323, 333 &343 K) were evaluated. The flask containing the samples were withdrawn from the shaker at predetermined time intervals, filtered and the final concentrations of MB dye in the supernatant solutions were analyzed using the UV-visible spectrophotometer (Model Hitachi – 2800). The pH of the solution was adjusted using 1M HCl or NaOH. The amount of equilibrium uptake of MB dye was determined using

$$q_e = \frac{(Co - Ce)V}{M} \text{--------------------------} 1$$

$$\%Dye\ Removal = \frac{(Co - Ce)V}{M} x100 \text{---------} 2$$

Where$q_e$is the amount of dye taken up by the adsorbent at equilibrium (mg/g), C_o is the initial dye concentration (mg/l), Ce is the dye concentration at equilibrium (mg/l), M is the mass of the adsorbent (g), and V is the volume of the solution, (L).

3. Theory

3.1. Adsorption Isotherm

Different adsorption isotherm models have been used to describethe sorption equilibrium. Langmuir, Freundlich, Harkins and Jura, Dubinin–Raduskevich (D–R), Halsey, and Temkin isotherm modelswere applied in the present study.

3.1.1. Langmuir Isotherm

The Langmuir model describes the monolayer adsorption. It assumes a uniform energy of adsorption, a single (homogenous) layer of adsorbed solute at a constant temperature [19, 20]. The linear form of Langmuir equation is given as

$$\frac{Ce}{qe}=\frac{1}{qmKl}+\frac{Ce}{qe} \text{ --------------------------3}$$

Where q_e (mg/g) is the amount of dye adsorbed at equilibrium, q_e (mg/g), the amount of dye adsorbed when saturation is attained, C_e is the equilibrium dye concentration (mg/l) and $K_l$is Langmuir constant related to the binding strength of dye onto the adsorbent.

3.1.2. Freundlich Isotherm

The Freundlich model is an empirical equation that is very useful in describing the distribution of solute between solid and aqueous phases at a point of saturation. The basic assumption of this model is that there is an exponential variation in site energies of adsorbent and also the fall in heat of adsorption is logarithmic [21].

The linearized form of Freundlich equation is expressed as

$$\log qe=\log Kf+\frac{1}{n}\log Ce \text{ ---------------------4}$$

Where $K_f$is the Freundlich constant that represents adsorption capacity and n is the strength of adsorption. The significance of n is as follows: n=1 (linear); n<1 (chemical process); n>1 (physical process) [22].

3.1.3. Harkins and Jura Isotherm

The Harkins and Jura adsorption isotherm model accounts for multilayer adsorption and can be explained by the existence of a heterogeneous pore distribution [19].

The Harkins and Jura equation can be expressed as

$$\frac{1}{qe2}=\frac{B}{A}-\frac{\log Ce}{A} \text{ ---------------------------5}$$

Where B and A are the isotherm constants and can be obtained from the intercept and slope of the plot of $1/q_{e2}$ versus $\log C_e$ respectively.

3.1.4. Halsey isotherm

The Halsey adsorption isotherm model is suitable for multilayer adsorption at a relatively large distance from the surface and the fitting of the experimental data to this equation attest to the heteroporous nature of the adsorbent. The Halsey adsorption isotherm model can be expressed as [23, 24]:

$$\ln qe=\frac{\ln k}{nH}-\frac{\ln(1/Ce)}{nH} \text{ --------------------6}$$

Where n_H and K are Halsey isotherm constants and can be obtained from the slope and intercept of the plot of $\ln q_e$ against $\ln(1/C_e)$.

3.1.5. Temkin Isotherm

Temkin isotherm model assumes that the fall in the heat of adsorption is linear rather than logarithmic as stated in Freundlich expression [19]. The heat of adsorption of all molecules in the layer would decrease linearly with coverage owing to the adsorbent/adsorbate interactions [25-27]. The linearized form of Temkin equation is expressed as

$$qe=B\ln KT+B\ln Ce \text{ --------------------7}$$

Where K_T (mol/l) is the equilibrium binding constant corresponding to maximum binding energy, B is the constant related to the heat of adsorption and the differential surface capacity for the dye sorption per unit binding energy. If the constant B is less than 8kJ/mol, it indicates a weak interaction between the adsorbate and adsorbent hence such adsorption can be expressed as physical adsorption [22, 28]

3.1.6. Dubinin-Radushkevich (D-R) Isotherm

The Dubinin-Radushkevich (D-R) isotherm model can be expressed as [22]:

$$\ln qe=\ln qs-\beta\varepsilon^{2} \text{ -------------------8}$$

Where β is a constant related to the mean free energy of adsorption per mol of the dye (mol^2kJ^{-2}) when it is transferred to the surface of the adsorbent from infinity in solution, q_s is the theoretical saturation capacity, ε is the Polanyi potential given as

$$\varepsilon = RT1n\,(1+1/C_e) \text{ ----------------9}$$

Where R ($J.mol^{-1}.K^{-1}$) is a gas constant, T (K) is temperature. By making certain assumptions, the mean energy of adsorption E, can be calculated from the β value employing, the relation.

$$E=\frac{1}{\sqrt{2\beta}} \text{ ------------------------10}$$

3.2. Adsorption Kinetics

The pseudo-first-order, pseudo-second-order, power function, Elovich and intraparticle diffusion kinetic models were applied to study the adsorption kinetics of MB and to compute the extent of uptake in the adsorption process.

3.2.1. Pseudo-First-Order Kinetic Model

The linear form of the pseudo-first-order kinetic mode is represented by

$$\ln(q_e - q_t) = \ln q_e - K_1 t \text{-----------------} 11$$

Whereq_e and q_t are the values of amount of the dye adsorbed per unit mass on the adsorbent at equilibrium and at various time t, respectively, K_1 is the Pseudo-first-order adsorption rate constant (min^{-1}). The values of K_1 and calculated q_e can be determined from the slope and intercept respectively, of the linear plot of $\ln(q_e - q_t)$ versus t.

3.2.2. Pseudo-Second-Order Kinetic Model

The pseudo-second-order kinetic model is expressed by

$$\frac{t}{qt} = \frac{1}{K2qe^{2}} + \frac{1}{qe}t \text{------------------------} 12$$

Where K_2 is the pseudo-second-order adsorption rate constant (g/mg/min) and q_e is the amount of dye adsorbed (mg/g) on the adsorbent at equilibrium. The initial adsorption rate, h ($mg.g^{-1}.min^{-1}$) is expressed as:

$$h = \kappa 2qe^{2} \text{-----------------------------} 13$$

The plot of t/q_t versus t gives a linear relationship which allow computation of k_2, h and calculated q_e..

Among these models, the criterion for their applicability is based on judgment on the respective correlation coefficient (R^2) and agreement between experimental and calculated value of q_e [12, 22, 29].

3.2.3. Elovich Kinetic Model

The linearized form of Elovich kinetic equation (model) is expressed by [19, 29].

$$qt = \frac{\ln(\beta\alpha)}{\beta} - \frac{Int}{\beta} \text{-------------------} 14$$

Where: ∝ is the initial adsorption rate ($mg.g^{-1}.min^{-1}$) and β is the desorption constant ($mg.g^{-1}min$) if the adsorption fits the Elovich model, a plot of q_t versus ln (t) should yield a linear relationship with a slope of (1/β) and an intercept of (1/β) ln (∝β).

3.2.4. Power Function Kinetic Model

The power function kinetic equation (model) is represented by [19].

$$\text{Log } q_t = \text{Log } a + b \log t \text{-----------------} 15$$

Where: the constant, a, represents the initial rate ($mg.g^{-1}.min^{-1}$) and the constant b represents the rate constant of the reaction (g/mg/min). If the adsorption fits the power function model, a plot of log q_t versus log t should yield a linear relationship witha slope of b and intercept log a.

3.2.5. Intra-Particle Diffusion Model

The intra-particle diffusion model is expressed by [12, 19]:

$$Q_t = Kit^{1/2} + C \text{---------------------} 16$$

Where: C is the intercept which represents the effect of boundary layer thickness and Ki is the intra particle diffusion rate constant ($mg.g^{-1}min^{1/2}$), which can be evaluated from the slope of a linear plot of q_t versus $t^{1/2}$.

If the plot of q_t versus $t^{1/2}$ gives a straight line, then the intra particle diffusion is involve in the adsorption process also if this line passes through the origin then the intra particle diffusion is the sole rate controlling step in the adsorption process. However, if the plot of q_t versus $t^{1/2}$ appears as multi linear plots, then two or more steps influence the adsorption process such as film diffusion and intra particle diffusion [12, 22, 30, 31].

3.3. Thermodynamic Parameters

The thermodynamic parameters such as change in Gibb's free energy change (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) were determined using the following equations:

The Gibb's free energy, ΔG^o, equation is expressed as follows [32, 33].

$$\Delta G = -RT\ln K_{ads} \text{---------------------------} 17$$

The equilibrium constants (K_{ads}) were calculated according to the following equation:

$$Kads = \frac{\overset{m}{(q\,e)}}{(Ce)} \text{----------------------------} 18$$

Where: R is gas constant ($8.314Jmol^{-1}K^{-1}$) and T is absolute temperature in Kelvin, qe^m is dye concentration on the solid at equilibrium and Ce is dye concentration in solution at equilibrium.

The Van't Hoff equation is expressed as follows [29, 32, 33]:

$$\ln Kads = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \text{------------------} 19$$

Where R is gas constant, T is absolute temperature in Kelvin, ΔS^o and ΔH^o are entropy and enthalpy respectively. The plot of $\log K_{ads}$ versus 1/T gives a linear relationship, which allows the computation of ΔH^0 and ΔS^o values from the slope and intercept respectively.

4. Results and Discussion

4.1. Adsorbent Characterization

The FTIR spectral of RCC powder obtained within the spectral range of 4000-500cm^{-1} as shown in Fig.1displayed all characteristics peaks of RCC such as prominent peak at

3857.76cm^{-1} due to hydroxyl group, OH, probably attributed to adsorbed water. The presence of O-H bond is confirmed by the non intense peak at 3257.88cm^{-1}. N–H bond could be ascribed to the band at 2376cm^{-1}. Peak at 2265.47cm^{-1} is due to C≡C bond, or C≡N bond. The peak at 1654.01cm^{-1}shows the presence of C=C bond from alkene. The –N-O bond from nitro-alkanes could be ascribed to the band at 1511.28cm^{-1}. The band at 1190.12cm^{-1} is due to the presence of C–N bond. The characteristics band at 1039.67 corresponds to C–O bond, confirming presence of carboxylic acid [12, 34, 35].

Also, Fig. 2 shows the SEM images of RCC powder. It can be observed from Fig. 2a that the external surface of RCC powder is uneven and irregular. On further magnification as indicated in 2b, the surface is very rough and contains heterogenous pores.

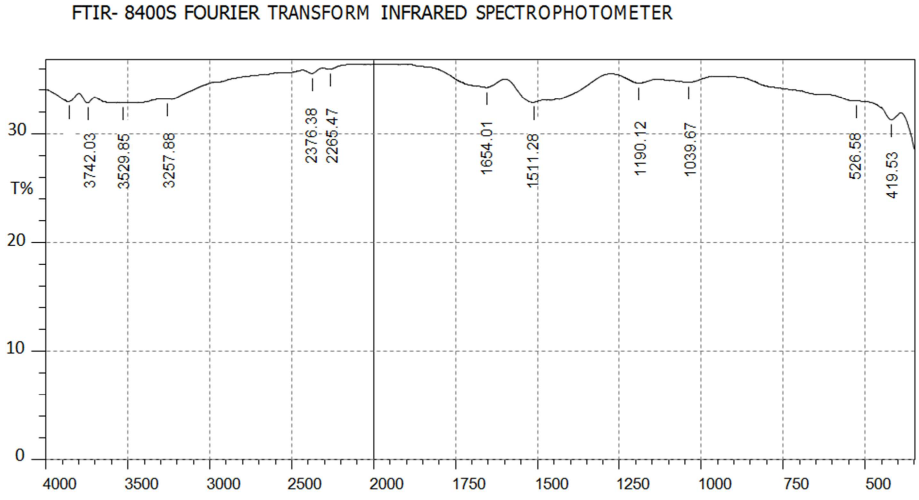

Fig. 1. *FTIR Spectra of RCC powder.*

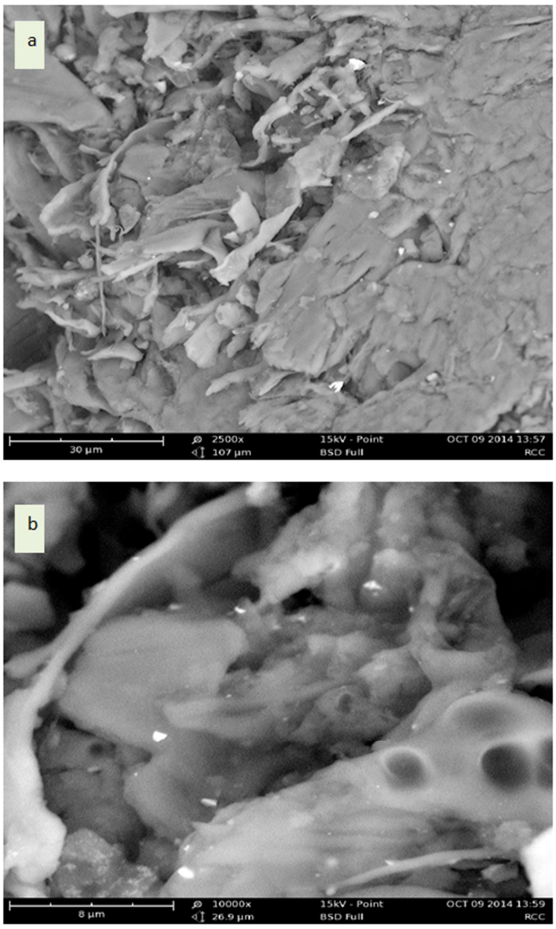

Fig. 2. *SEM micrographs of RCC powder surface (a) magnification 2500× and (b) magnification 10000×.*

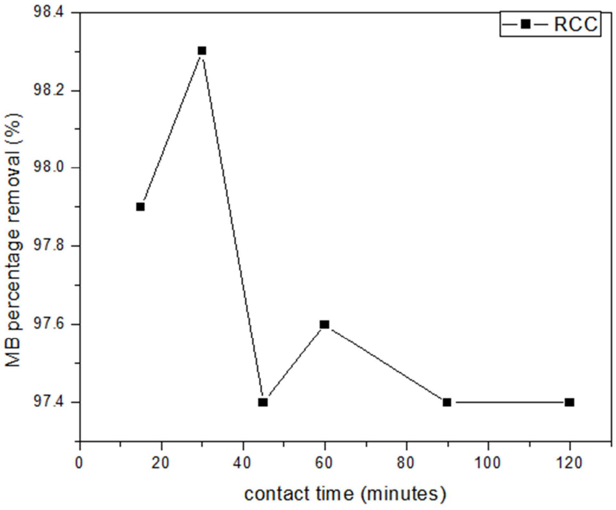

Fig. 3. *Effect of contact time on percentage removal of MB dye (MB concentration: 100mg/l, adsorbent dosage: 1.0g, volume of solution: 100ml temperature: 300±1 K).*

4.2. Effect of Contact Time

Contact time is an important parameter in the adsorption process. The effect of contact time on the removal of MB dye is depicted in Fig. 3. It can be observed that there was a rapid removal in the first 15 minutes and it proceeds slowly until optimum adsorption (equilibrium time) at 30 minutes. Later it decreases. Similar result has been reported for the adsorption of MB onto Neem leaves powder [36]. It can be inferred from the rapid sorption rate at the initial stages that there were abundance of active sites on the external surface of RCC which resulted in the rapid MB dye removal. The slower rate of removal at the later stages can be attributed to the diffusion of the dyes into the interior part of the adsorbent since the external surface has been occupied by the molecules of the dye (2). Once equilibrium is attained, there was no further increase due to the fact that the remaining vacant sites are difficult to occupy probably caused by repulsive forces between the molecules on the adsorbents and the bulk phase [37, 38].

4.3. Effect of Adsorbent Dosage

The effect of adsorbent dosage on the percentage removal of MB dye is depicted in Fig.4. It can be observed that the removal efficiency of MB dye increased with increase in adsorbent (RCC) dosage. This observation can be attributed to the fact that the availability of adsorption sites on adsorbent surface increased with the increase in the adsorbent dosage [39, 40]. Although the percentage removal of MB dye increased with increase of adsorbent dosage, the equilibrium adsorption capacity decreased with increase of adsorbent dosage (figure not shown). This may be due to overlapping or aggregation of the adsorption sites which limits the availability of all the active sites during adsorption process [29, 41]. Similar trend has been reported by El-Maghraby and El-Deeb [39] for the adsorption of MB using rice hulls.

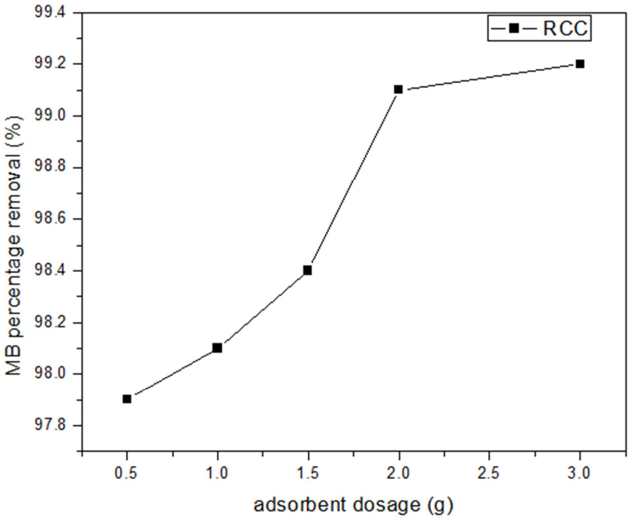

Fig. 4. *Effect of adsorbent dosage on percentage removal of MB dye (MB concentration: 100mg/l, contact time: 30mins, volume of solution: 100ml and temperature 300±1K).*

4.4. Effect of Initial Dye Concentration

The effect of initial MB dye concentration is depicted in Fig. 5. It can be observed that the percentage removal of MB dye increased with increase in initial concentration. This observation may be due to the fact that with increase in dye concentration, more dye molecules are available for adsorption by the adsorbent. This is attributed to the effect of concentration gradient which is the main driving force for the adsorption process [42]. Similar trend has been reported by Asiagwu *et al.* [43]. Furthermore, the equilibrium adsorption capacity increased with increase in initial dye concentration (figure not shown).This is attributed to the fact that increasing dye concentration increases the driving force to overcome all mass transfer resistances of the MB between the aqueous and solid phase, leading to an increase in equilibrium adsorption capacity [22, 44].

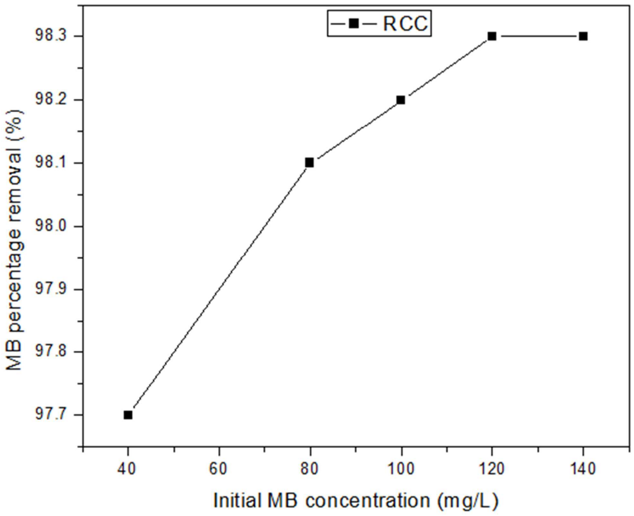

Fig. 5. *Effect of initial concentration on percentage removal of MB dye (Contact time: 30mins, Adsorbent dosage: 1g, volume of solution: 100ml and temperature 300±1K).*

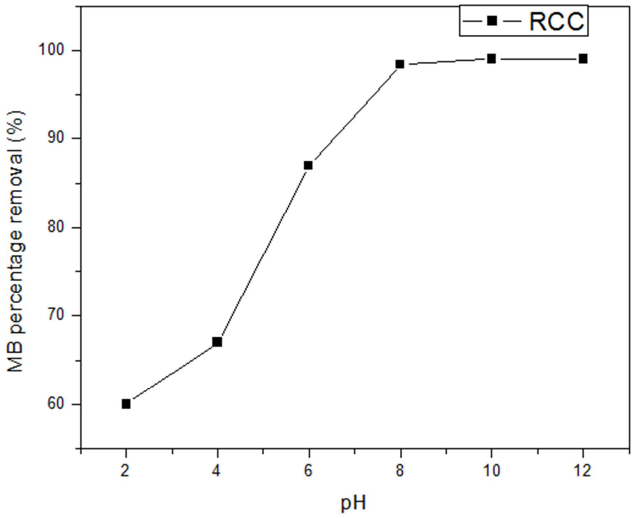

Fig. 6. *Effect of pH on percentage removal of MB dye (contact time: 30mins, MB concentration: 100mg/l, adsorbent dosage: 1g, volume of solution: 100ml and temperature 300±1K).*

4.5. Effect of pH

The pH of the dye solution is an important parameter in the adsorption process and the initial pH of dye solution has greater significance compared to the final pH of the solution in adsorption reaction [45]. The influence of pH on the adsorption of MB onto RCC is illustrated in Fig. 6. It was observed that the percentage removal of MB by RCC increased as the initial pH of the solution increased from 2 to 12. Similar trend have been observed by Soni *et al.* [7] for the adsorption of MB by water Hyacinth root powder. Optimum removal efficiency was obtained at pH of 10.0. The decrease in removal efficiency at lowpH can be attributed to the fact that at low pH values of the solution, the presence of excess hydrogen ion in the solution competes with the cationic groups of the MB dye for the adsorption sites on the adsorbent surface [46]. However, at higher pH values, the positive charges (H^+) at the solution interphasedecreases and the adsorbent surface is more negatively charged, thus enhancing electrostatic attraction of the cations of the MB dye leading to more removal efficiency.

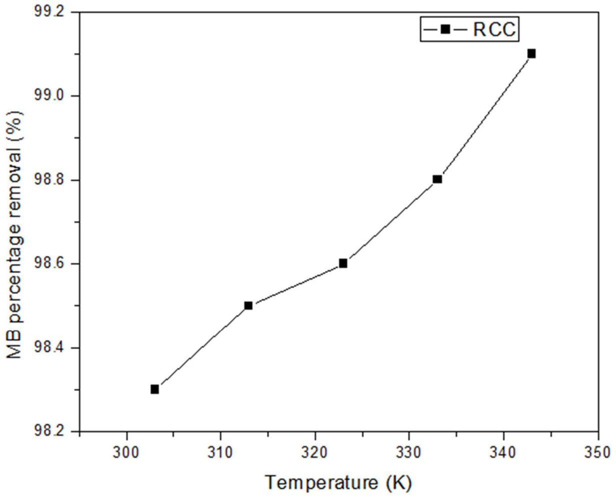

Fig. 7. *Effect of temperature (MB concentration: 100m/l, adsorbent dose: 1g, volume of solution: 100 ml and contact time: 30 mins).*

4.6. Effect of Temperature

The influence of temperature on the removal efficiency of MB by RCC is illustrated in Fig. 7. It can be observed (from Fig. 7) that increase in temperature resulted in increase in percentage removal of MB by RCC. Similar trend has been reported by Saja et al. [47] for the adsorption of basic dye by Kaolin. This increase in percentage removal with increase in temperature can be attributed to increase in both the mobility of the dye molecules and the number of active sites for the adsorption; hence the adsorption is an endothermic process [48].

4.7. Adsorption Isotherms

Six adsorption isotherm models were applied to describe the relationship between the MB dye concentration in the bulk solution and that on the RCC powdersurface namely: the Langmuir, Freundlich, Harkins and Jura, Dubinin–Raduskevich (D–R), Halsey, and Temkin isotherm models.

The plots of the various isotherms are shown in Figs. (8-11). The values obtained from the intercept and slope for each plot was summarized in Table 1. By comparing the linear square regression correlation coefficient, R2 (Table 1), the experimental data fitted well to both Freundlich and Halsey isotherm models.Furthermore, the Freundlich isotherm constant,*n*, (Table 1) was found to be less than 1 indicating that the adsorption of MB by RCC is a chemical process [22]. These observations evidence the adequacy of the Freundlich isotherm to describe the adsorption of MB onto RCC powder and such adsorption mainly occurred on the heterogeneous surface of the RCC powder.

The Dubinin – Radushkevich isotherm model for the adsorption of MB onto RCC is depicted in Fig. 9. From the high values of correlation coefficient (R^2) as shown in Table 1, the D – R isotherm was found to be a good fit for the adsorption of MB by RCC powder. The maximum MB dye sorption capacity of RCC powder was found to be 18.28 mg/g.

The Temkin isotherm model for the adsorption of MB onto RCC is illustrated in Fig. 10 and the Temkin parameters are calculated and summarized in Table 1. It can be observed from Table 1, that the Temkin model was also a good fit for the adsorption of MB onto RCC powder. Thehigh value of correlation coefficient (R^2) reflects the adequacy of Temkin model in explaining the adsorption of MB onto RCC. Furthermore, from Table 1, it can be observed that the values of heat of adsorption, B, was found to be (greater than) > 8 kJ/mol, which indicates a strong interaction between the MB dye and RCC powder, thus the process can be expressed as chemical adsorption [28].

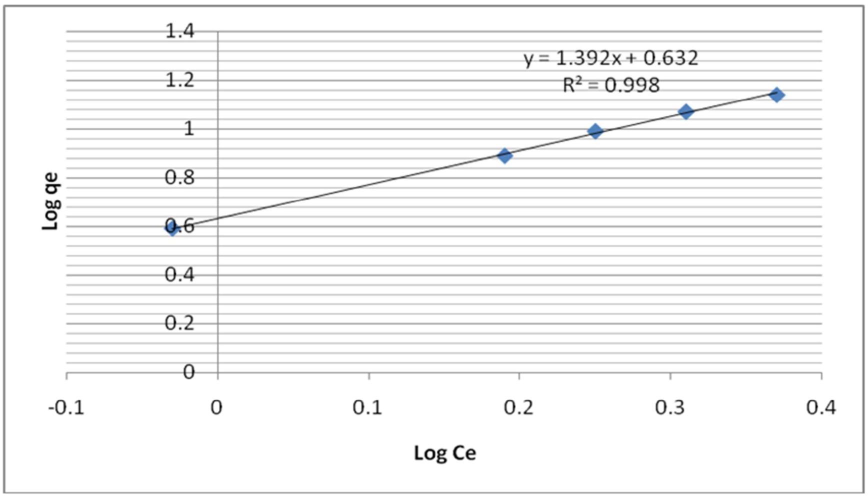

Fig. 8. *Freundlich adsorption isotherm for MB dye on RCC.*

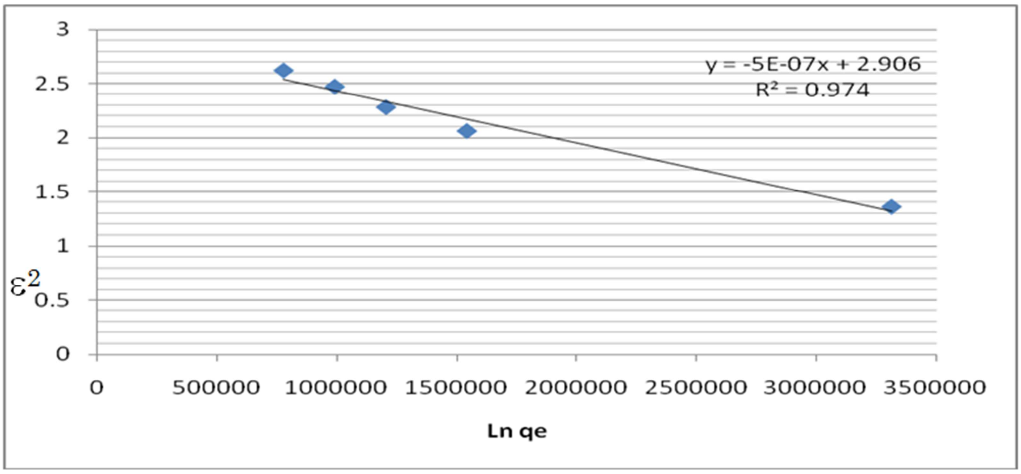

Fig. 9. *D–R plot for adsorption of MB onto RCC.*

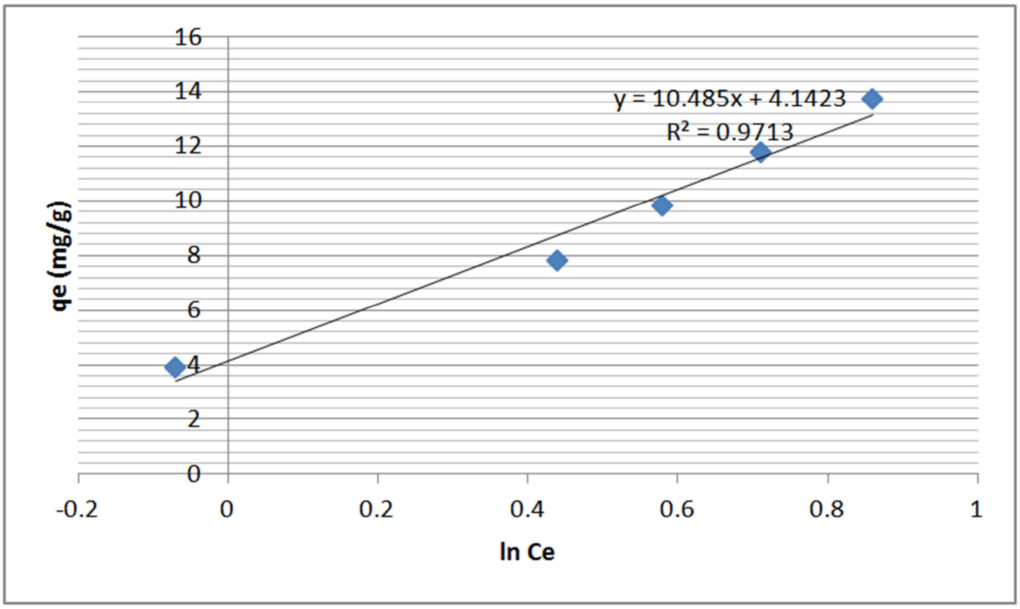

Fig. 10. *Temkin isotherm model for MB adsorption onto RCC.*

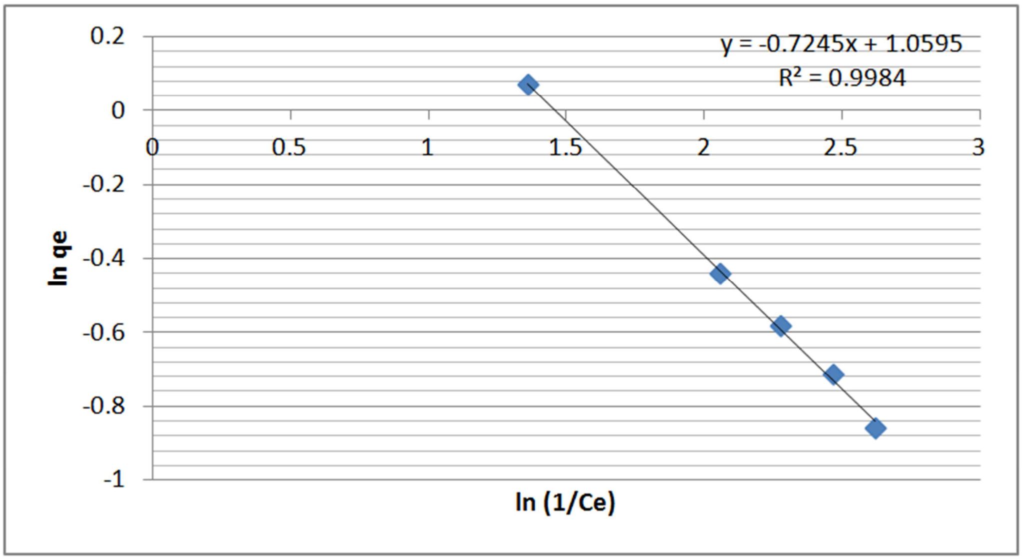

Fig. 11. *Halsey isotherm model for MB adsorption onto RCC.*

Table 1. *The Isotherm Parameters and Values of Correlation Coefficient for the Adsorption of MB onto RCC powder.*

Langmuir	q_m(mg/g)	K_L	R^2
	-20.41	-1.77	0.929
Freundlich	$K_{F\ (mg/g)(L/mg)}{}^{1/n}$	n	R^2
	4.285	0.718	0.998
D-R	$q_{s\ (mg/g)}$	$\beta_{\ (mol}{}^2KJ^{-2})$	R^2
	18.28	5.0×10^{-7}	0.974
Harkins & Jura	A	B	R^2
	6.289	0.346	0.915
Halsey	K	n_H	R^2
	4.31	1.38	0.998
Temkin	B (KJ/mol)	K_T (mol/L)	R^2
	10.48	1.484	0.971

4.8. Adsorption Kinetics

Five kinetic models i.e., pseudo-first-order, pseudo-second-order, power function, Elovich and intraparticle diffusion model as mentioned earlier were applied to investigate the reaction pathways and potential rate determining steps of the adsorption of MB dye onto raw corn cobs powder.

The pseudo-first-order model did not provide a good fit to the experimental data. The first-order rate constant, k_1, the correlation coefficients, R^2 and the theoretical and experimental equilibrium adsorption capacity q_e are given in Table 2. The plot of log (q_e- $q_{t)}$ versus t (not shown) was non linear with low R^2 (0.321). Moreover, the theoretical and experimental equilibrium adsorption capacity q_e obtained from the plot did not agree (i.e., varied widely), suggesting the inadequacy of the pseudo-first-order model for describing the adsorption kinetics of MB dye onto raw corn cobs powder.

Furthermore, the kinetic data was fitted to the pseudo-second-order model. The pseudo-second-order rate constant, k_2, the initial adsorption rate, h and the theoretical and experimental equilibrium adsorption capacity are given in Table 2. The plot of t/q_t against t is depicted in Fig.12. Contrary to the pseudo-first-order model, the fitting of the kinetic data in the pseudo-second-order model showed excellent linearity with high correlation coefficients, R^2. In addition, there was good agreement between the calculated q_e and the experimental q_e values (i.e., the q_e values were close) indicating that the adsorption of MB by raw corn cobs powder followed the pseudo-second-order kinetics. Hence the adsorption process is controlled by chemisorptions [12, 49]. This suggests that the forming of interaction between the adsorbate and the adsorbent on the external surface of the adsorbent (film diffusion) is the rate determining step [2].

The power function model did not provide a good fit to the experimental data. The power function constants, a, b and the correlation coefficients, R^2 are given in Table 3. The plot of log q_t versus log t (not shown) was non linear with low R^2 suggesting that the power function model was not appropriate for describing the adsorption of MB onto raw corn cobs powder.

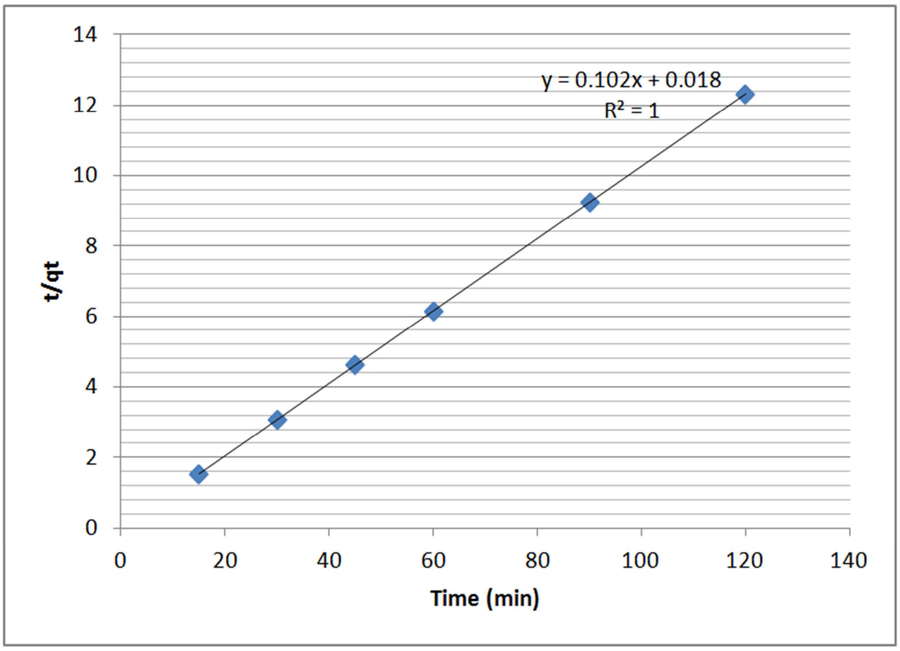

Fig. 12. *Pseudo second-order plot for adsorption of MB onto RCC.*

The Elovich model did not provide a good fit to the experimental data. The Elovich constants,α, β and the correlation coefficients are given in Table 3. The plot of q_t against ln t (figure not shown) was also non linear with low R^2 suggesting that the Elovich model was not appropriate for describing the adsorption of MB onto raw corn cobs powder.

The intraparticle diffusion (Weber Morris) model was evaluated to identify the adsorption mechanism. The Weber Morris constant, $k_{i,}$ and C are given in Table 3. The Weber Morris plot for the adsorption of MB onto raw corn cobs powder (figure not shown) was non linear and do not pass through the origin suggesting that intraparticle diffusion was not the rate limiting step. The large intercept indicate the great contribution of surface sorption in the rate limiting step [29, 30].

Table 2. *Pseudo-first and second order kinetic model parameters, equilibrium adsorption capacity and values of correlation coefficient for CV dye adsorption onto RCP.*

Pseudo-First Order Model				**Pseudo-Second Order Model**			
q_e (exp) (mg/g)	**k_1 ($g.mg^{-1}min^{-1}$)**	**q_e(cal) (mg/g)**	**R^2**	**H ($mg.g^{-1}min^{-1}$)**	**K_2 ($g.mg^{-1}min^{-1}$)**	**q_e(cal) (mg/g)**	**R^2**
9.84	0.013	0.0265	0.321	55.56	0.578	9.80	1.00

Table 3. *Intra-particle, Elovich, and Power function model parameters with their values of correlation coefficient for CV adsorption onto RCP.*

Intraparticle diffusion			**Elovich Model**			**Power Function**		
K_{id}	**C**	**R^2**	**β**	**α**	**R^2**	**A**	**B**	**R^2**
mg/g/min	**mg/g**		**$g.min^{-1}$**	**$mg.g.mg^{-1}$**		**$g.mg^{-1}min^{-1}$**	**$g.mg^{-1}min^{-1}$**	
0.01	9.840	0.504	22.73	5.269×10^{96}	0.498	9.89	0.003	0.456

4.9. Adsorption Thermodynamics

The linear Van't Hoff equation plot for the adsorption of MB onto RCC powder is shown in Fig. 13. Table 4, presentsΔH^o and ΔS^o values obtained from the Van't Hoff plot including the calculated ΔG^o values. negative ΔG^o values obtained at all temperatures (Table 4) indicate the feasibility and the spontaneous nature of MB adsorption onto RCC powder. It was observed that the values of ΔG^o for the adsorption of MB onto RCC decreased with increase in temperature suggesting a rapid and more spontaneous adsorption at the lower temperature. The positive ΔH^o value confirms the endothermic nature of the adsorption process. The positive value of ΔS^o reveals increased randomness at the solid/solution interfaces and good affinity of the adsorbent (RCC) for the MB dye [32, 50].

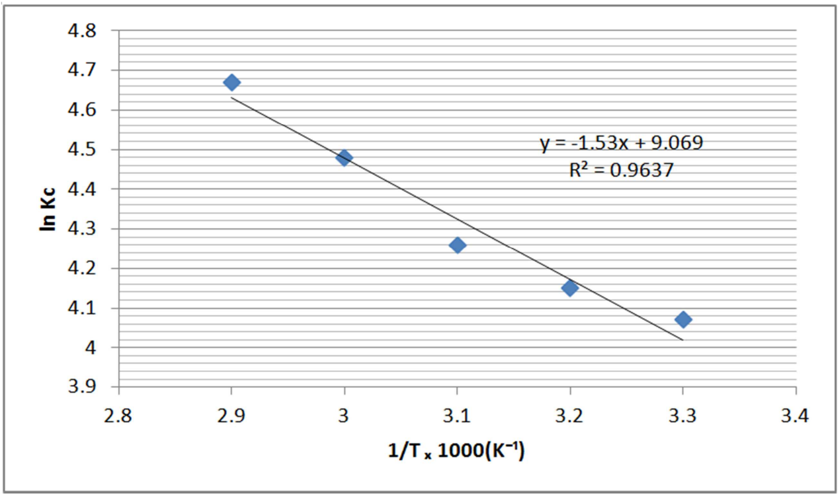

Fig. 13. *Van't Hoff plot for the adsorption of MB onto RCC powder.*

Table 4. *Thermodynamic parameters for the adsorption of CV dye on RCC.*

Temperature (K)	**ΔG (KJ/mol)**	**ΔH (KJ/mol)**	**ΔS (J/mol. K)**
303	-10.25	12.720	75.40
313	-10.80		
325	-11.43		
333	-12.40		
343	-13.32		

5. Conclusion

The potential of Raw Corn cobs (RCC) powder as an effective adsorbent for the removal of MB dye from aqueous medium has been identified. The adsorption of MB onto RCCpowder was found to be influenced by contact time, adsorbent dose, initial MB concentration, temperature and initial pH of the solution. The optimum adsorption of MB dye was found at pH 10. Maximum adsorption capacity was 18.28mg/g at 100mg/L initial MB concentration. Temperature had strong influence on the adsorption process and the maximum removal was observed at 343K. The equilibrium was attained at 30 min, after which there was no increase in MB adsorption. The kinetic studies revealed that the adsorption process followed the pseudo-second-order kinetic model. Intraparticle diffusion was not the rate determining step. The study on equilibrium sorption revealed that Freundlich and Halsey isotherm model gave the best fit to the experimental data.The nature of adsorption of MB onto RCC powder was chemical adsorption as inferred from Freundlich isotherm model and Temkin isotherm model. The calculated thermodynamic parameters indicated a spontaneous and endothermic nature of the adsorption of MB dye onto RCC powder. The present study showed that RCCpowder can be effectively used as an inexpensive and efficient adsorbent without any pretreatment or modification for the treatment of dye effluents or waste water.

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