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Sorption Isotherm Studies for the Removal of Brilliant Blue Dye from Aqueous Solution by Modified Egyptian Kaolin

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ABSTRACT--- ***In this study, the adsorption of Brilliant Blue G-250 (BBG), cationic dye onto Kaolin and modified – kaolin samples was investigated. Kaolin was used as a raw material to prepare three different adsorbents through chemical modification by using nitric acid, polyvinyl alcohol and a mixture of polyvinyl alcohol with nitric acid. Characterization studies were performed using XRD, FTIR, SEM, BET surface area and pore structure. Batch adsorption studies were carried out to evaluate the effect of adsorbent dose (0.1 – 0.4g), initial dye concentration (50 - 250 mg/L) and temperature (298 – 333K) on the adsorption capacity of BBG dye. The experimental equilibrium adsorption data was represented using two – parameter isotherm models including Langmuir, Freundlich, Elovich, Temkin, Halsey, Harkin – Jura and Flory – Huggin isotherms. Adsorption isothermal data satisfactorily fits with the Langmuir model and the maximum adsorption capacity was found to be 50mg/g for the kaolin sample modified with nitric acid. Thermodynamic studies showed that the dye adsorption is exothermic and a spontaneous process. These results indicate that modification of kaolin could be promising as a cheap adsorbent for the removal of BBG dye from aqueous solutions.***

Keywords--- Kaolin, cationic dye, acid activation, polyvinyl alcohol, isotherms

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1. INTRODUCTION

The introduction of waste products in the environment is a worldwide problem that has been highlighted in the past decades. Discharging of dyes into water resources can cause environmental damage as the dyes give water an undesirable color [1] and reduce sunlight penetration, with some dyes also being toxic/ carcinogenic [2]. A number of technologies have been developed and used for removal of the dye contaminants from wastewater; including oxidation processes, nanofiltration, ozonation, and coagulation [3-6]. However, these processes are found to be infeasible for an industrial application due to their low efficiency, high operating cost and environmental impact [7].

Adsorption is one of the prominent methods used in wastewater treatment for dye removal due to its simplicity in operation and availability of a wide range of adsorbents. The increasing demand of efficient and economical treatment technology has given rise to a search of alternative low cost adsorbents to substitute the use of commercial activated carbon that are expensive and difficult to be regenerated.

Among the alternative low – cost adsorbents, clay adsorption is considered as the most economical option for dye removal [8]. Clay is composed mainly of silica, alumina and water, frequently with appreciable quantities of iron, alkalis and alkali earths [9]. Two structural units are involved in the atomic lattices of most clay minerals. One unit consists of closely packed oxygen and hydroxyls in which aluminum, iron and magnesium atoms are embedded in an octahedral combination. The second unit is built of silica tetrahedrons. Clays are classified by the differences in their layered structures. There are several classes of clays such as smectites (montmorillonite, saponite), mica (illite), kaolinite, serpenite, polyphyllite (talc), and sepiolite.

Clays have a high adsorption capacity due to their lamellar structure which provides high specific surface areas [10] and possibility to adsorb ions and polar organic molecules or particle external site an in inter layer positions [11, 12]. Adsorption and desorption of organic molecules in the clays are primarily controlled by surface properties of the clay and the chemical properties of the molecules [13]. Some of the clays are either used in their natural state or beneficiated before usage through processes such as calcinations, acid activation, pillaring, anion and cation exchange organic modification with polymers or molecules [14]. Natural clay exhibits a negative charge of structure which allows it to adsorb positively charged dyes but induces a low adsorption capacity for anionic dyes. Thus literature mostly reports on cationic dye ad- sorption by clay [15, 16] and very few studies have been devoted to anionic dye absorption onto natural clay [17, 18]. In aqueous solution, cationic dyes carry a net positive charge due to the presence of protonated amine or sulpher containing cationic dyes, like those used in this work, can be attracted towards the anionic layers and are, therefore, quite suitable for investigating the properties of these minerals in aqueous suspensions.

Kaolin is a dioctahedral 1:1 layered clay mineral of structural formula $Al_2Si_2O_5(OH)_4$. Each layer consists of two sheets: a tetrahedral sheet in which silicon atoms are tetrahedrally coordinated by oxygen atoms; and an octahedral sheet where aluminium atoms are octahedrally coordinated to hydroxyl groups and shared apical oxygens from the silica tetrahedral sheet. Kaolin is referred to as clay that is mainly composed of Kaolinite and a lower amount of minerals such as quartz and mica. The adsorption properties of kaolinite are likely determined by its surface structure and the edges [19]. The edges posses a variable charge that can be correlated to the reaction between ionisable surface groups along the edges and the clay mineral surface and the ions present in aqueous solution.

Polyvinyl alcohol (PVA) is a water soluable hydrophilic polymer with characteristics of non – toxicity, biocompatibility and biodegradability [20]. It consists of one hydroxyl in each repeat unit with being crosslinkable representing desirable adsorbent structure. The basic properties of PVA are dependent on the degree of polymerization or on the degree of hydrolysis. In this study, PVA is used as a modifying agent onto kaolin.

The objective of this paper is to evaluate the adsorption capacity of kaolin to remove BBG-250 from water. The research focused on evaluating how the initial dye concentration, adsorbent dosage, pH and temperature. The best – fit equilibrium isotherms were determined by studying various isotherm models. Adsorption kinetic models were also employed to analyze the kinetics. Thermodynamics were also applied to examine the adsorptive tendency of these materials.

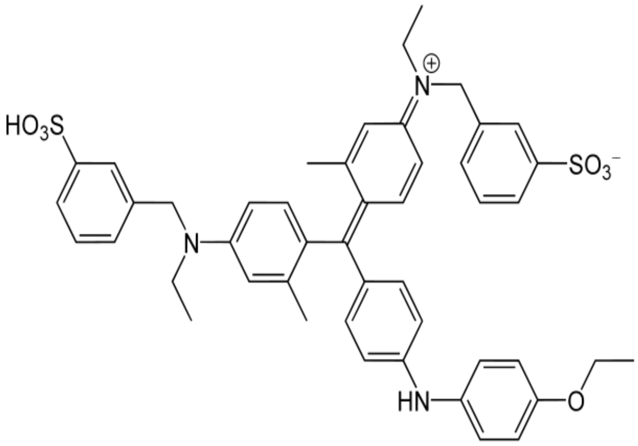
2. EXPERIMENTAL

2.1 Materials

Egyptian Kaolin, hydrated aluminium silicate, was collected from Sinai (Saint Catherine) which is considered as the main source of kaolin in Egypt [21].On collection, stones and other heavy particles were removed from the samples. Poly (vinyl alcohol) (PVA) was purchased from Fisher Chemical. Brilliant Blue G-250 (Coomassie Brilliant Blue G-250) was obtained from Aldrich Chemical company, Inc. All other chemicals were of analytical grade and were used in as- received state without further purification.

2.2 Preparation of dye solution

The basic dye, Brilliant Blue G-250 (CI. 42655, chemical formula $C_{47}H_{50}N_3NaO_7S_2$, M.W: 856.13gmol^{-1}, λ_{max}: 620 (at pH= 2). The chemical structure of the dye is illustrated in Fig. (1). A stock solution 250 mgL^{-1} was prepared by dissolving 0.25g of dye in a 1000 ml of distilled water. The serial dilutions (20-100mgL^{-1}) were prepared by diluting the stock solution in accurate proportions. Batch adsorption studies were performed at room temperature. The pH of the solutions was adjusted by using 0.1N NaOH or 0.1N HCl using a pH meter.



Properties	
Chemical formula	$C_{47}H_{50}N_3NaO_7S_2$ (Sodium salt)
Molar mass	856.03 g/mol
Solubility in water	Slightly soluble in cold, soluble in hot (bright blue)
Solubility in ethanol	Soluble

Figure 1: Molecular structure and chemical properties of dye

2.3 Preparation of PVA solution

PVA solution (10% w/v) was prepared by dissolving 50g of PVA in distilled water with constant stirring for 2h and heating around 90ºC.

2.4 Preparation of kaolin and modified kaolin samples

Egyptian kaolin used in this study was collected from Sinai (Saint Catherine and Dehessa), which is considered as the main source of kaolin in Egypt. A portion of the raw kaolin in a 1L beaker was maintained in suspension in doubly de- ionized water for several hours. The sample was then centrifuged and dried at 373K. The unmodified kaolin is designated as K. The kaolin under investigation was then divided into three portions. The first portion was prepared by taking 50g of kaolin with 100 ml distilled water and heating to boiling then treated with 2M HNO3. The resulting mixture was rapidly agitated until formation of gel by raising the temperature of the suspension to 343 K. The temperature of the system was then increased to 353K and another 5% PVA was added to generate a coating. This procedure was repeated three times before the sample was washed thoroughly with distilled water and dried in an oven at 333K. This sample is abbreviated as MKN. The second portion was treated with 10% PVA/ formaldehyde solution by the same procedure as given in the previous steps and designated as MKP. The third portion under investigation was treated with 2M HNO_3 then followed by 10 % PVA / formaldehyde solution. After treatment, the resulting solution was washed several times with deionzed water then subjected to vacuum filtration and dried in an oven at 373K. This sample was designated as MKNP.

2.5 Characterization of the clay adsorbents

The Fourier Transform Infrared Spectroscopy Analysis (FTIR) was carried out using KBr pellets (2mg of sample to 200mg of KBr). The analysis was carried out in the range between 4000 and 400cm^{-1}. The specific surface area of all samples under investigation was determined through adsorption / desorption of nitrogen at -196°C using the Brunauer - Emmet - Teller method. The samples were first degassed at 200°C for 2h before each measurement was recorded. The morphological features of the modified – clay samples were obtained from Scanning Electron Microscopy (SEM) using Philips scanning microscope at an accelerating voltage of 10 KV. The samples were coated with gold by electrodeposition under vacuum prior to analysis. The X - ray diffraction analysis (XRD) was carried out in a Phillips diffractometer with angular variation of 2Ө, CoK$_{\alpha}$ radiation=1.78Å.

2.6 Batch equilibrium studies

Adsorption experiments were performed using the standard batch technique. The concentration of the residual dye was measured using UV- Vis spectrophotometer at λ= 620nm. Calibration curve was plotted between absorbance and concentration of the dye solution to obtain absorbance – concentration profile. The amount of dye adsorbed at equilibrium was calculated using the following equation:

$$q_e = \frac{(C_o - C_e)V}{W} \qquad (1)$$

where q_e (mg/ g) is the equilibrium adsorption capacity per unit weight of adsorbent, C_o and C_e (mgL^{1-}) are the initial and equilibrium concentration of BBG in the solution, respectively, V (L) is the volume of the solution and W(g) is the mass of adsorbent used.

The percentage removal of dye was calculated using the following relationship:

$$\%\text{color removal} = \frac{C_o - C_t}{C_o} \times 100 \qquad (2)$$

where C_o and C_t (mg/L) are the initial dye concentration and concentration at time t, respectively.

3. RESULTS AND DISCUSSION

3.1 Characterization of the investigated samples

Surface area and pore size of adsorbents are among important parameters that describe the quality of adsorbents. Table (1) shows the BET surface area, pore volume (V_p) and pore diameter (r) for the kaolin and different modified clay samples under investigation. From the Table, it can be shown that all samples belong to the mesopore region according to the IUPAC classification. Also, acid impregnation increased the specific surface area of kaolin from 102 m^2 /g to 115 m^2 /g. However, impregnation with PVA led to a decrease in the specific surface area. It has been reported that during acidification, the octahedral ions can be leached out and led to an increase in the specific surface area [22].The micropore volume results are also given in Table (1). It can be seen that acid modification improved the development of micropores, however, PVA led to a decrease in porosity due to blockage of pores on the surface of the sample.

Table (1): Surface area and pore characteristics of the kaolin and modified samples

Adsorbent	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore diameter (nm)
K	102	0.035	11
MKN	115	0.02	14
MKP	59	0.04	10
MKNP	108	0.025	13

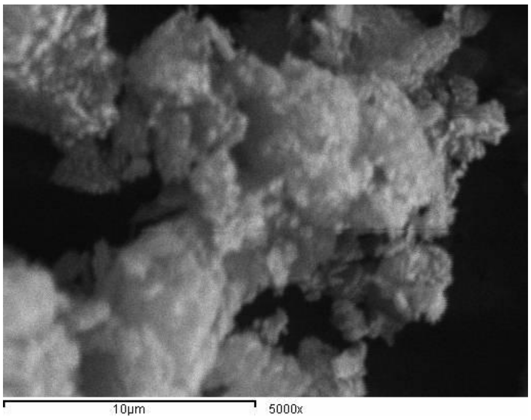
The FT-IR spectroscopy technique is an important tool for identifying characteristic functional groups which are capable of adsorbing dye ions. The tabulated data for FTIR spectra band assignments for kaolin and modified samples are presented in Table (2). It can be seen that the spectra obtained exhibit similarities, although a minimum diminution in the intensity bands is noted, relating to the distortion and flexability of the tetrahedral and octahedral layers that make up the structure of clay minerals due to modification [23]. Researchers designated band at 3859 – 3620 due to stretching vibration of - OH groups as the fingerprint bands of kaolinite[24].The –OH bending region of kaolinite shows vibrations of the inner surface OH groups at 913 cm^{-1}; additional bands near 755 cm^{-1} are associated with surface hydroxyls [25]. Also, bands assigned at 1006, 1034 and 1108 cm^{-1} are due to SiO – stretching frequencies, bands at 535 – 540 cm^{-1} are assigned to Si-O-Al bending frequencies where the Al is in octahedral coordination. Comparison between the IR spectrums show the appearance of three new bands for the sample treated with HNO3 at 2972 cm^{-1}, 1939 cm^{-1} and 1537 cm^{-1} which is attributed to N – H – O stretching and N – H in plane bending, respectively. Two additional intense new bands appeared at 1381 cm^{-1} and 754 cm^{-1}. These bands are assigned to C – N stretch and NO_2 bonding entrance of aromatic nitro group, respectively [26].

Table (2): Vibrational frequencies and assignments for the adsorption of kaolin and modified kaolin samples

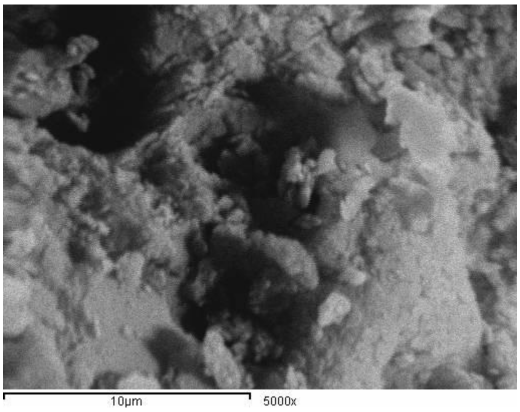
Band (cm^{-1})	Assignments
3859 - 3620	- OH stretching (internal)
3449	- OH stretching (internal)
2927 - 1939	- N – H – O stretching
2856	- CH stretching
1537	- N – H plane bending
1381	- C – N stretching
1825	- OH bending
1006, 1034, 1108	- Si-O stretching
754	- NO_2 bending
535 – 540	- Si-O-Al bending

X-ray diffraction (XRD) is a basic technique to determine the bulk structure and compositions of materials with crystalline structure. The X – ray diffraction of the pure and modified kaolin samples show that the mineralogical composition of the clay was found to contain predominately kaolinite (55%) and quartz minerals (36%). In all the samples, two intense diffraction at 2Θ value of 12.6°and 26.7°, less intense peaks at 38.5° 45.5°, 48.0°,and 60.3° which are all associated with kaolinite. However, diffraction peaks of quartz could be found at 2Θ values of 21.5°, 36.7°, 51°, and 60° and 68°.No significant shift in the d- spacing and diffraction angle (2Θ) was observed for all the samples investigated which implies that the modification does not affect the internal structure of the clay mineral [27].

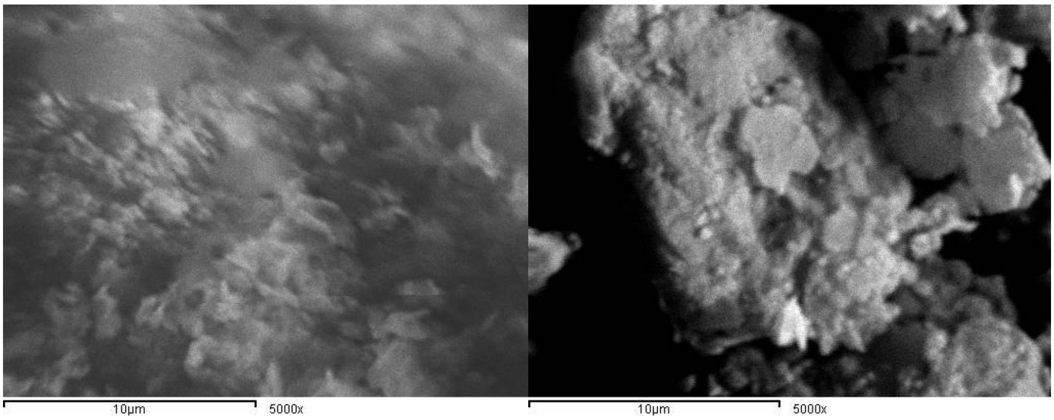
The surface morphology of the pure and modified kaolin samples was observed using SEM analysis. The SEM images are shown in Fig.(2). The micrograph of the untreated sample suggests solid flakes piled up on top of one another, however the sample modified with nitric acid shows rarely formed pore structure. The micrograph of the sample treated with PVA suggests the creation of pores and noticeable cage – like cavities while that modified with PVA and nitric acid shows that no pores could be detected and was in a highly amorphous form. It is suggested that the pores were diminished during modification [28].



Kaolin



MKP



MKNP MKN

Figure 2: SEM micrograph for kaolin and different modified samples

Effect of initial dye concentration

The effect of initial BBG concentration (50 – 250 ppm) on the adsorption capacity of the modified clay adsorbents was investigated at pH 2 and 298K. Experimental results are shown in Fig. 3 for the adsorption of BBG onto the different investigated clay samples. From the figure, an increase in the initial dye concentration led to an increase in the adsorption capacity. It can be proposed that an increase in the initial dye concentration leads to an increase in mass gradient between the solution and adsorbent, thus acts as a driving force for the transfer of dye molecules from bulk solution of the particle surface. The increase in the proportional dye adsorption is attributed to the equilibrium shift during the clay adsorption process [29].

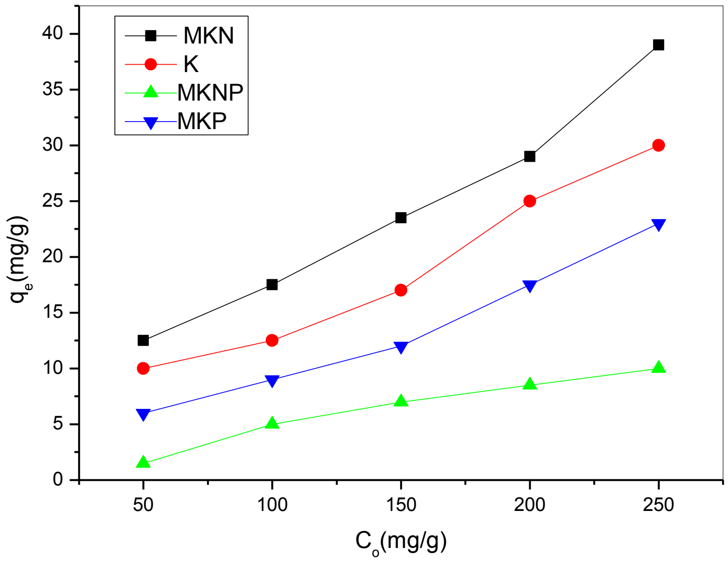


Figure 3: Effect of dye concentration on kaolin and modified kaolin samples

3.3. Effect of adsorbent dosage

The effect of adsorbent dosage ranging from 0.1-0.4g on the BBG removal (50 mg l^{-1}) over various modified clay samples is represented in Fig. (4). It was observed that the removal efficiency increases with increasing the adsorbent dosage. This implied that the number of adsorption sites increase as adsorbent mass increased. This can be attributed to the increase in the adsorbent surface area and availability of more adsorption sites. In this system, 40mg was used as optimal amount for further experiments.

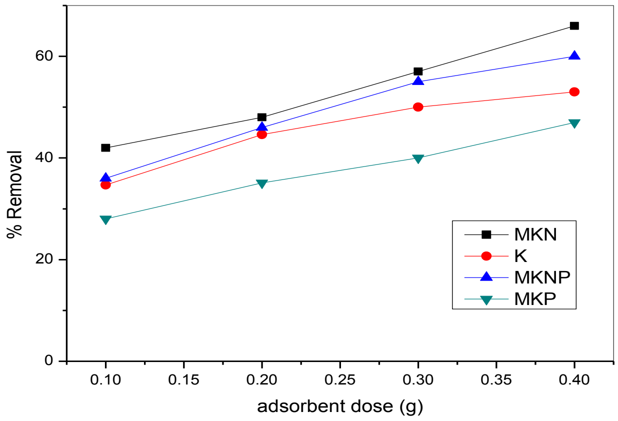


Figure 4: Effect of adsorbent dose on kaolin and modified kaolin samples

3.4 Adsorption Isotherm

Analysis of adsorption isotherm is of fundamental importance to describe how adsorbate molecules distribute between the liquid phase and the solid phase when the adsorption process reaches equilibrium [30]. In order to optimize the design of an adsorption system for removing the dye, it is important to establish the most appropriate condition for the equilibrium curves.

The equilibrium isotherms used to describe the BBG- Kaolin (liquid – solid) adsorption system are Langmuir, Freundlich, Elovich, Halsey, Temkin, Flory – Huggins and Harkin – Jura isotherms. Linear regression is used to determine the best – fitting isotherm and the applicability of isotherm equations is compared by judging the correlation coefficients.

3.4.1. Langmuir Isotherm

The basic assumption of Langmuir model is the formation of monolayer adsorption onto a completely homogenous surface with finite number of identical sites and negligible interaction between the adsorbed molecules. Based upon these assumptions, the linear form of Langmuir is represented as follows [31]:

$$\frac{c_e}{q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m} \quad \dots\dots\dots\dots\dots\dots\dots..(1)$$

where K_L is the Langmuir adsorption constant (L/mg), Q_m is the theoretical maximum adsorption capacity (mg/g). C_e is the equilibrium concentration of adsorbate (mg/L). The value of Q_m and K_L constants were calculated from the slope and intercept of the plot (C_e/q_e Vs. C_e) and presented in Fig.(5) and tabulated in Table 3. The essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant R_L which is defined by the following equation:

$$R_L = \frac{1}{1 + K_L C_e} \quad \dots\dots\dots\dots\dots\dots\dots.(2)$$

The value of R_L indicates the type of isotherm to be either unfavorable ($R_L>1$), linear ($R_L=1$), favorable ($0<R_L<1$) or irreversible (R_L=O). The R_L values found in the present study were in the range 0.01-0.02 indicating that adsorption of BBG by different modified clay samples was favorable.

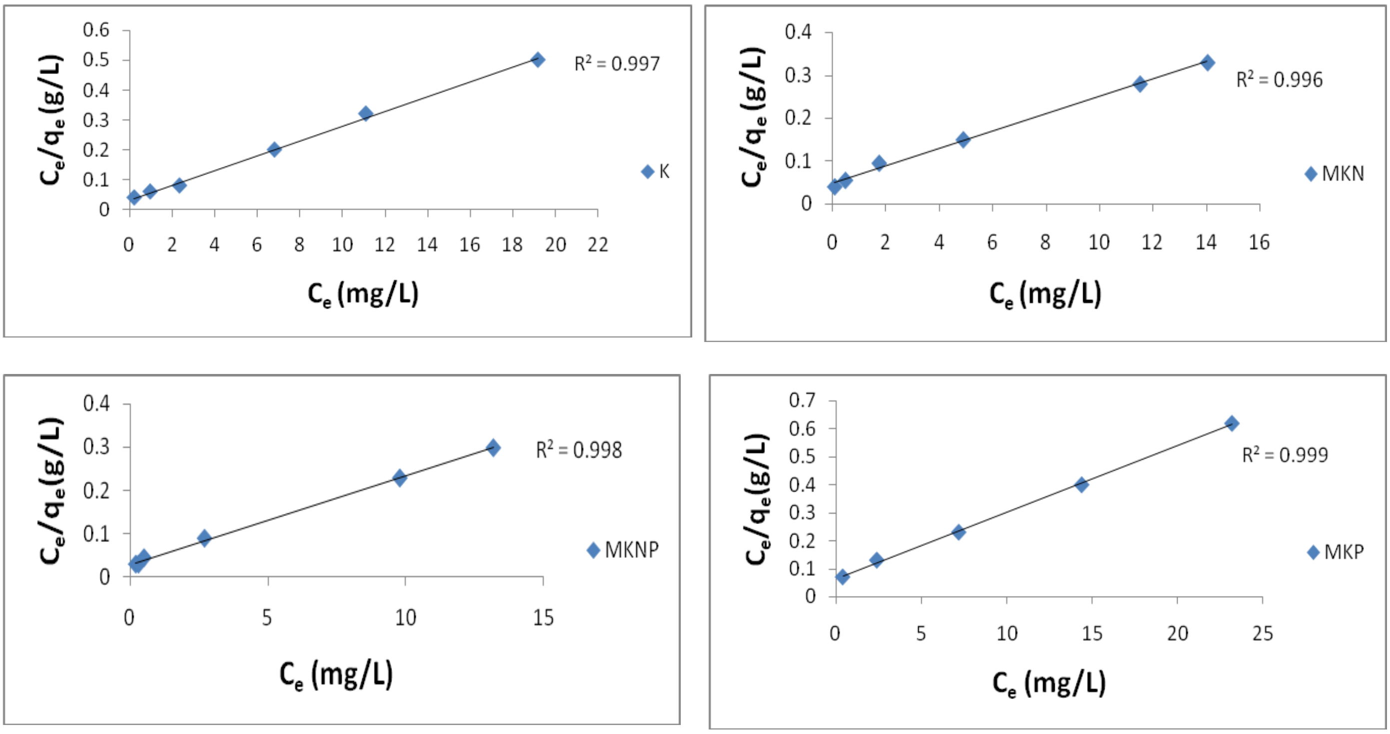


Figure 5: Langmuir isotherms model for BBG adsorption onto kaolin and modified kaolin samples

3.4.2. Freundlich Isotherm

The Freundlich model [32] assumes that the sorption takes place on heterogeneous surfaces with a non – uniform distribution of heat of sorption over the surface. It can be expressed in the linear form as follows:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \quad \dots\dots\dots\dots\dots (3)$$

where q_e is the equilibrium amount of adsorbate adsorbed by the solid (mg/g), C_e is the equilibrium concentration of adsorbate (mg/L), K_F is the Freundlich equilibrium constant (L/mg), and $\frac{1}{n}$ is indicative of the energy or intensity of the reaction and suggests the favorability and capacity of the adsorbent / adsorbate system. The constants K_F and 1/n are determined from the plot of log q_e Vs. log C_e (Fig.6). The favorable absorption of this model can be characterized such that if a value for n is above unity, adsorption is favorable and is physical process [32]. In the present study, the value of n is greater than 1, indicating that the adsorption process is favorable. The results are illustrated in Table 3.

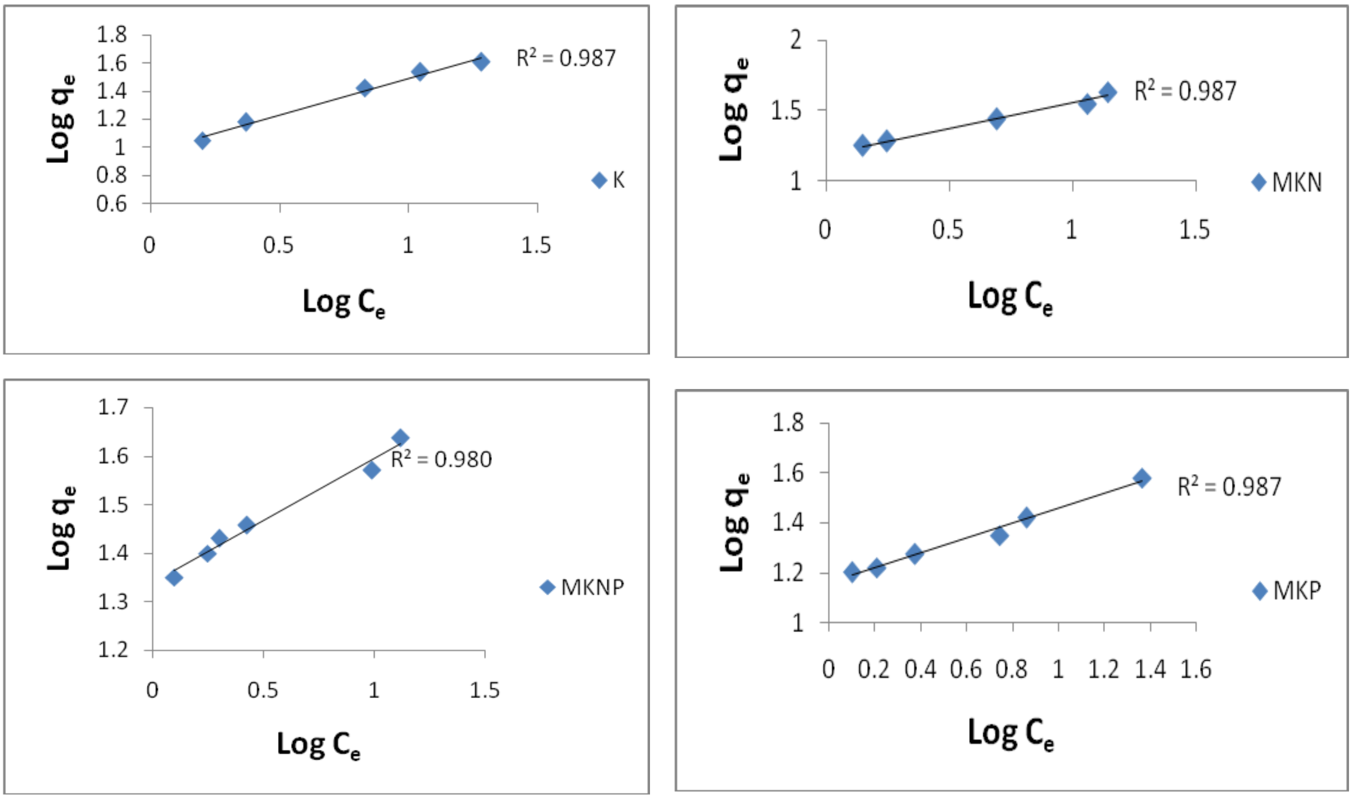


Figure 6: Freundlich isotherms model for BBG adsorption onto kaolin and modified kaolin samples

3.4.3 Elovich Isotherm

The Elovich [33] model is based on a kinetic principle assuming that the adsorption sites increase exponentially with adsorption, which implies a multilayer adsorption. The linear form of the equation is expressed as:

$$\ln\frac{q_e}{C_e} = \ln k_E q_m - \frac{1}{q_m} q_e \qquad \dots\dots\dots\dots\dots\dots (4)$$

where K_E is the Elovich equlibrim constant ($Lmol^{-1}$) and q_m is the Elovich maximum adsorption capacity ($molg^{-1}$). If the adsorption obeys Elovich equation, Elovich maximum adsorption capacity and Elovich constant can be calculated from the slopes and the intercepts of the plot Ln (q_e/C_e) V_s. q_e (Fig. 7). The results are illustrated in Table 3.

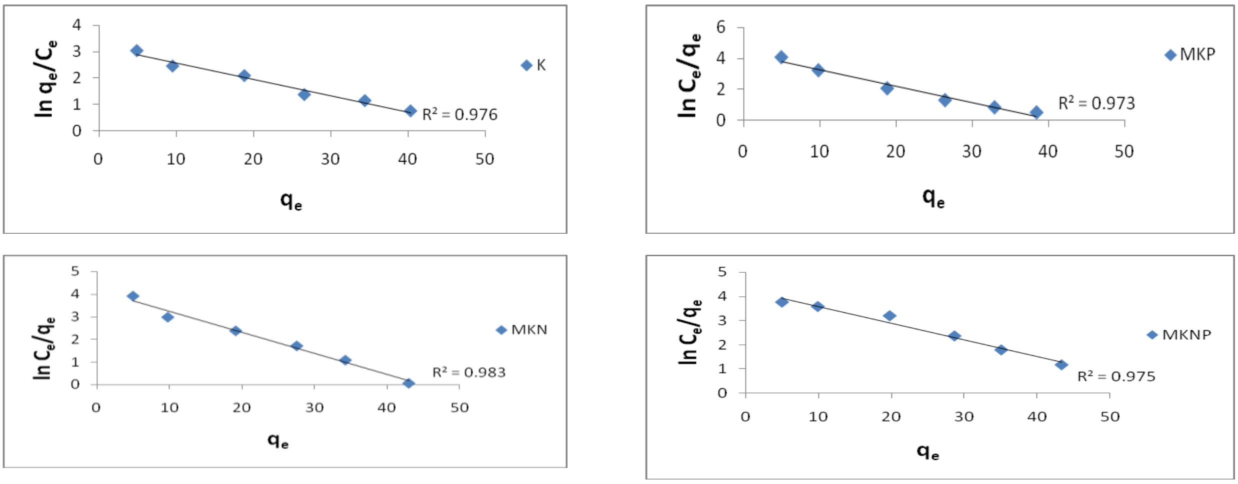


Figure 7: Elovich isotherms model for BBG adsorption onto kaolin and modified kaolin samples

3.4.4. Temkin Isotherm

Temkin [34] considered the effects of some indirect adsorbate / adsorbate interactions on adsorption isotherms. This model assumes that the heat of adsorption (function of temperature) of all molecules in the layer would decrease straightly with coverage when the lowest and the highest values of concentration are ignored. The linearized form of the Temkin model is represented as follows:

$$q_e = \frac{R_T}{B_T}\ln A_T + \frac{R_T}{B_T}\ln C_e \ldots\ldots\ldots\ldots\ldots\ldots.(5)$$

where q_e is the fractional coverage, R is the universal gas constant (8.314 KJ/ K mol), T is the temperature (K), K_T is the Temkin equilibrium binding constant (L/mg), and B_T is the variation of adsorption energy (KJ/ mol). Values of K_T and B_T were calculated from the intercept and slope of the plots of q_e versus ln C_e (Fig.8). The results are illustrated in Table 3.

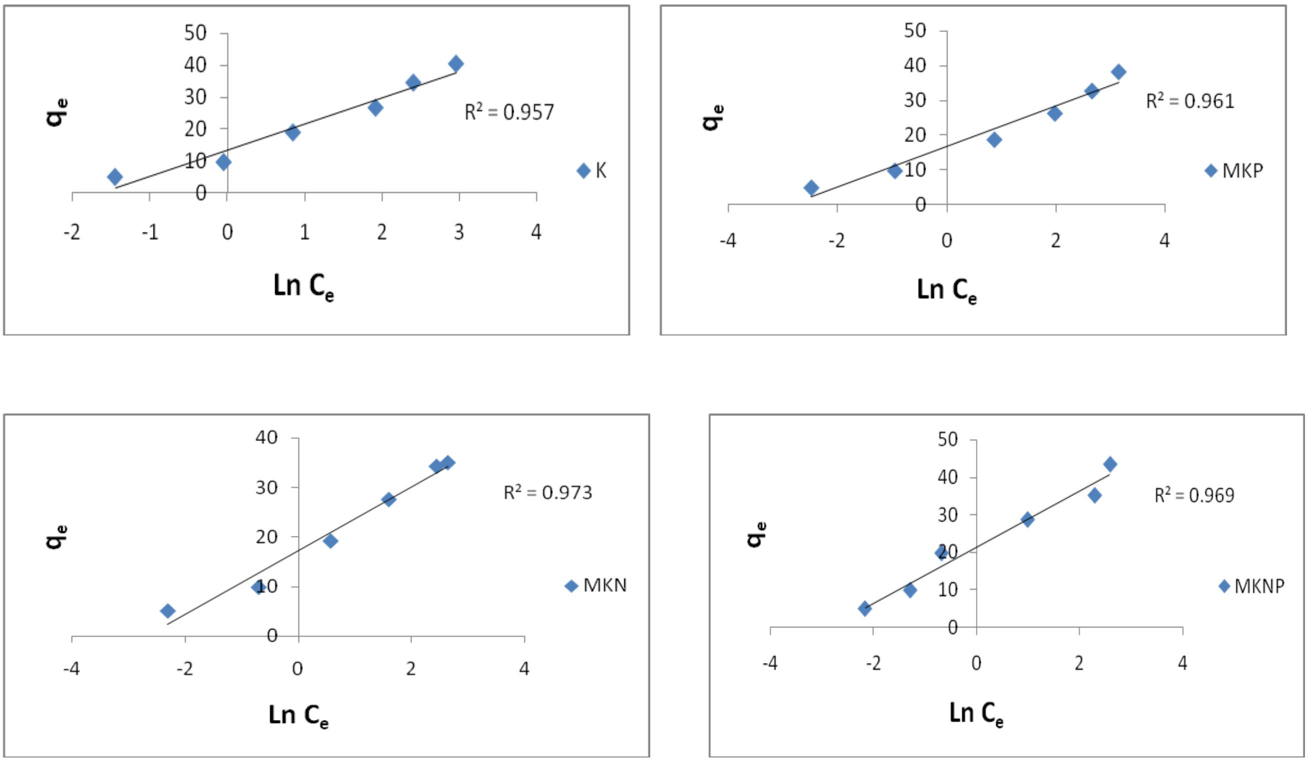


Figure 8: Temkin isotherms model for BBG adsorption onto kaolin and modified kaolin samples

3.4.5. Halsey Isotherm Model

The Halsey isotherm model [35] is suitable for multilayer adsorption at a relatively large distance from the surface. The fitting of the experimental data to this equation explains the heterogonous nature of the adsorbent. The Halsey model can be expressed as follows:

$$\ln q_e = \frac{1}{n_H}\ln k_H - \frac{1}{n_H}\ln C_e \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

Where K_H and n_H are the Halsey isotherm constants which can be determined from the plot of ln q_e versus ln C_e (Fig.9). Isotherm constants and correlation coefficients are listed in Table (3).

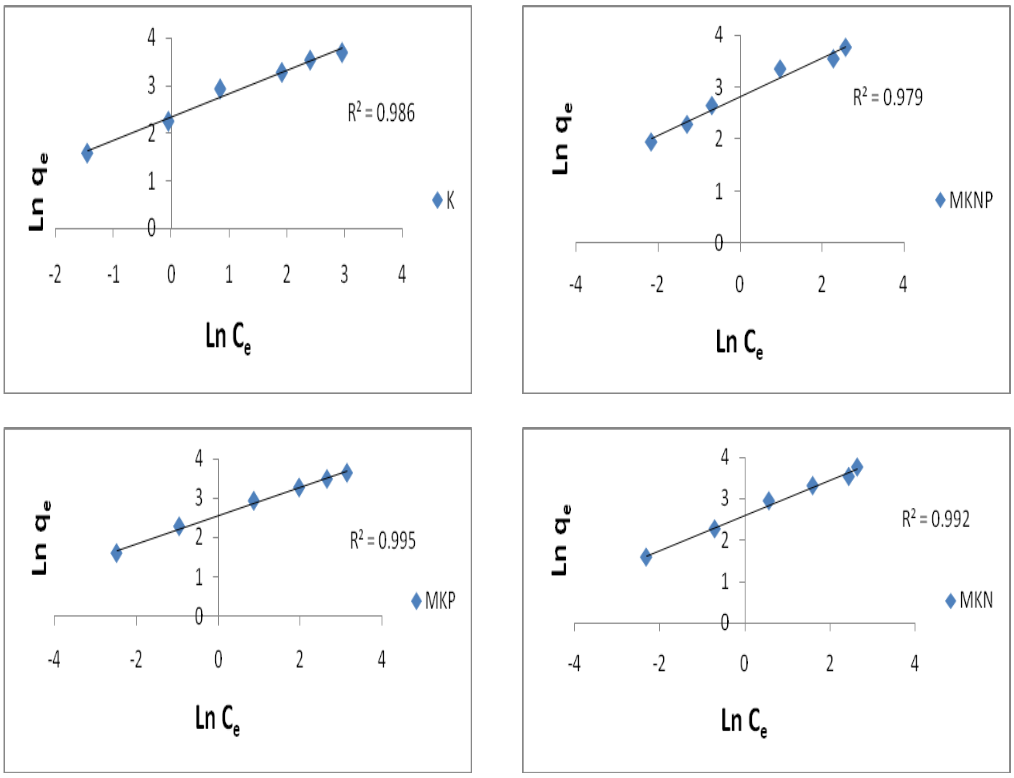


Figure 9: Halsey isotherms model for BBG adsorption onto kaolin and modified kaolin samples

3.4.6. Harkin – Jura Isotherm Model

The Harkin – Jura adsorption [36] isotherm describes multi- layer adsorption and can be explained with the existence of heterogeneous pore distribution. The equilibrium data can be analyzed using the following equation:

$$\frac{1}{q_e^2} = \frac{B}{A} - \frac{1}{A}\log C_e \qquad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots . (7)$$

where C_e (mg/L) is the equilibrium concentration of dye in solution, q_e (mg/g) is the amount of dye adsorbed on to the adsorbent, B and A are the isotherm constants which can be determined by plotting $\frac{1}{q_e^2}$ versus log C_e from the straight line (Fig.10). The H-J constants and correlation coefficient (R^2) value confirms that the H- J isotherm is less accurate in explaining the adsorption of BBG onto the modified clay samples (Table 3).

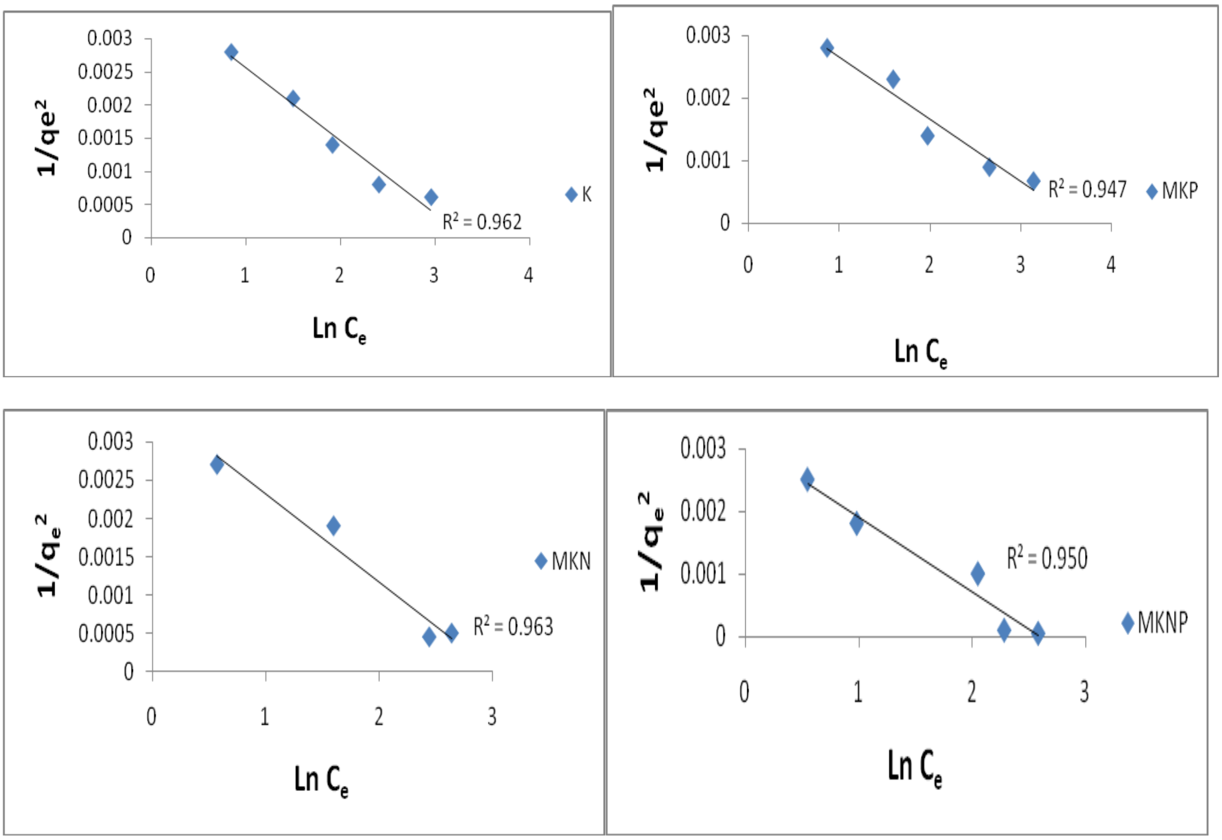


Figure 10: Harkin Jura isotherms model for BBG adsorption onto kaolin and modified kaolin samples

3.4.7. Flory – Huggin Isotherm Model

The Flory - Huggins model [37] was used to determine the degree of surface coverage characteristics of the adsorbate on the adsorbent . The linear form of the equation is expressed as:

$$\ln\frac{\theta}{C_\circ} = \ln K_{FH} + n\ln(1-\theta) \ldots\ldots\ldots\ldots\ldots\ldots (8)$$

where θ is the surface coverage of the adsorbent by the adsorbate ($\theta = 1 - C_e/C_o$), n is the number of dye occupying adsorption site, K_{FH} (L/mol) is the Flory - Huggins equilibrium constant, C_o and C_e are the initial and equilibrium concentration of BBG dye in solution respectively. A plot of ln θ/C_o versus ln(1-θ) (Fig.11) gives a straight live which enables the calculation of the constants from the slope and intercept of the plot. The results are tabulated in Table 3.

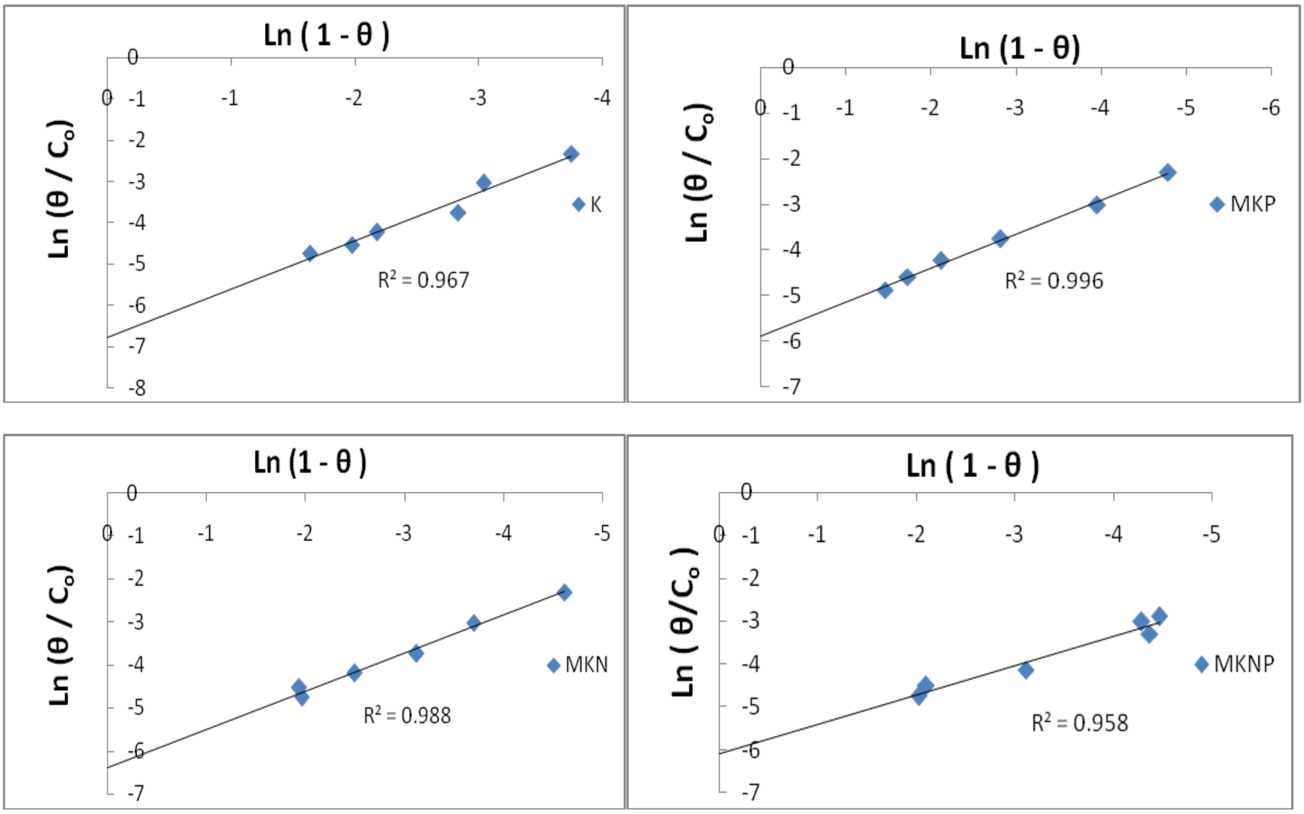


Figure 11: Flory – Huggins isotherms model for BBG adsorption onto kaolin and modified kaolin samples

Based on the correlation coefficient for all isotherm models studied, Langmuir model gave the highest R^2 value showing that the adsorption of BBG onto the different modified day samples was best described by this model followed by Halsey, Freundlich, Elovich, Temkin, Flory Huggins isotherm models while Harkin Jura isotherm model presented poor fit of the experimental data than the other isotherms.

3.5. Effect of Temperature

The effect of temperature on adsorption capacity of the different modified clay samples at pH 2 and dye concentration 250mgL was studied over series of temperature at 298, 313, and 333K (Fig. 12). It is observed from the figure, that the adsorption capacity decreased by increasing the temperature. This indicates that the adsorption of BBG dye onto the different modified samples is exothermic in nature. The decrease in adsorption with rise in temperature may be due to the weakening of adsorptive force between the active sites of the adsorbent and the adsorbed species. The optimum temperature was found to be 298 K within the temperature range studied.

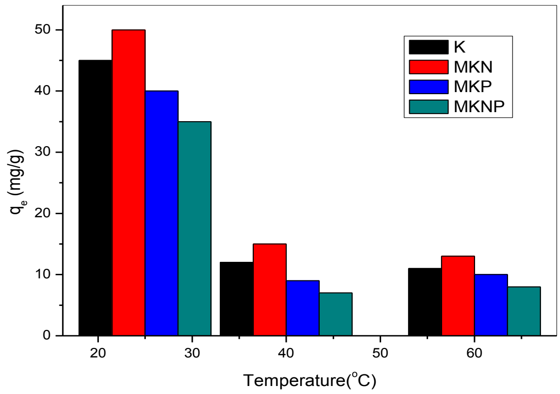


Figure (12): Effect of temperature on**to** kaolin and modified kaolin samples

Table (3): Values of isotherm constants for the adsorption of BBG onto kaolin and modified kaolin samples

Isotherm model	K	MKN	MKP	MKNP
Langmuir				
Q_m(mg/g)	41.6	50.0	35.7	45.4
K_L (l/mg)	0.8	0.4	0.5	0.9
R^2	0.99	0.99	0.99	0.99
Freundlich				
K_F	13.2	17.4	13.8	21.4
1/n	0.37	0.31	0.33	0.23
R^2	0.98	0.98	0.98	0.98
Halsey				
K_H	1.32×10^2	4.58×10^2	8.96×10^2	5.0×10^2
n	2.0	2.4	2.7	2.2
R^2	0.98	0.99	0.99	0.98
Elovich				
q_m	14.5	11.6	9.3	9.8
K_E	1.2	1.4	1.6	1.7
R^2	0.97	0.98	0.97	0.97
Temkin				
K_T	5.4	13.6	5.7	26
B_1	320	323	344	424
R^2	0.95	0.96	0.96	0.95
Flory – Huggins				
K_{FH}	1.2×10^{-3}	1.5×10^{-3}	3.0×10^{-3}	1.8×10^{-3}
n	1.4	0.9	0.8	0.8
R^2	0.97	0.98	0.99	0.96
Harkin – Jura				
A	639	2364	538	1032
B	2.3	7.7	2.1	1.6
R^2	0.96	0.95	0.95	0.95

3.6. Thermodynamic study

Thermodynamic parameters were evaluated to confirm the adsorption nature of the present study. The thermodynamic constants, free energy change (ΔG^o), enthalpy change (ΔH^o) and entropy change (ΔS^o) were calculated to evaluate the thermodynamic feasibility and spontaneous nature of the process. Therefore the thermodynamic constants can be obtained from the following equations:

$$\Delta G = - RT \ln K_L \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

$$\Delta G = \Delta H^o - T\Delta S^o \quad \ldots\ldots\ldots\ldots\ldots\ldots.. \quad (10)$$

in which K_L is defined as Langmuir's equilibrium constant (L/mol). ΔH^o is the enthalpy change and ΔS^o is the entropy change. Combining equations (9) and (10), gives Van't Hoff equation which enables the calculation of enthalpy change and entropy change.

$$\text{Ln}\, K_L = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (12)$$

ΔH^o and ΔS^o can be obtained from the Van't Hoff plot of Ln K_L versus 1/T. The thermodynamic parameters are listed in Table 4 and represented in Fig. (13). The negative ΔG values confirm the spontaneous nature and feasibility of the adsorption process. The ΔG^o values decreased as the temperature increased from 298 to 333K, which is an indication of the physical adsorption nature of the process. The positive values of ΔS^o suggests the increased randomness at the solid – solution interface during the adsorption of BBG on the modified clay samples. The positive values of ΔH^o confirm the exothermic nature of the adsorption process.

Table (4): Thermodynamic parameters for the removal of BBG onto kaolin and modified kaolin samples

Adsorbent	ΔG(KJ/mol)			ΔH(KJ/mol)	ΔS (J/mol/K)
	298	313	333		
K	-33.3	-31.7	-30.3	-58.1	83.1
MKN	-31.5	-31.0	-28.8	-53.4	66.5
MKP	-32.0	-28.1	-28.9	-57.0	79.0
MKNP	-33.5	-31.6	-30.4	-62.8	83.1

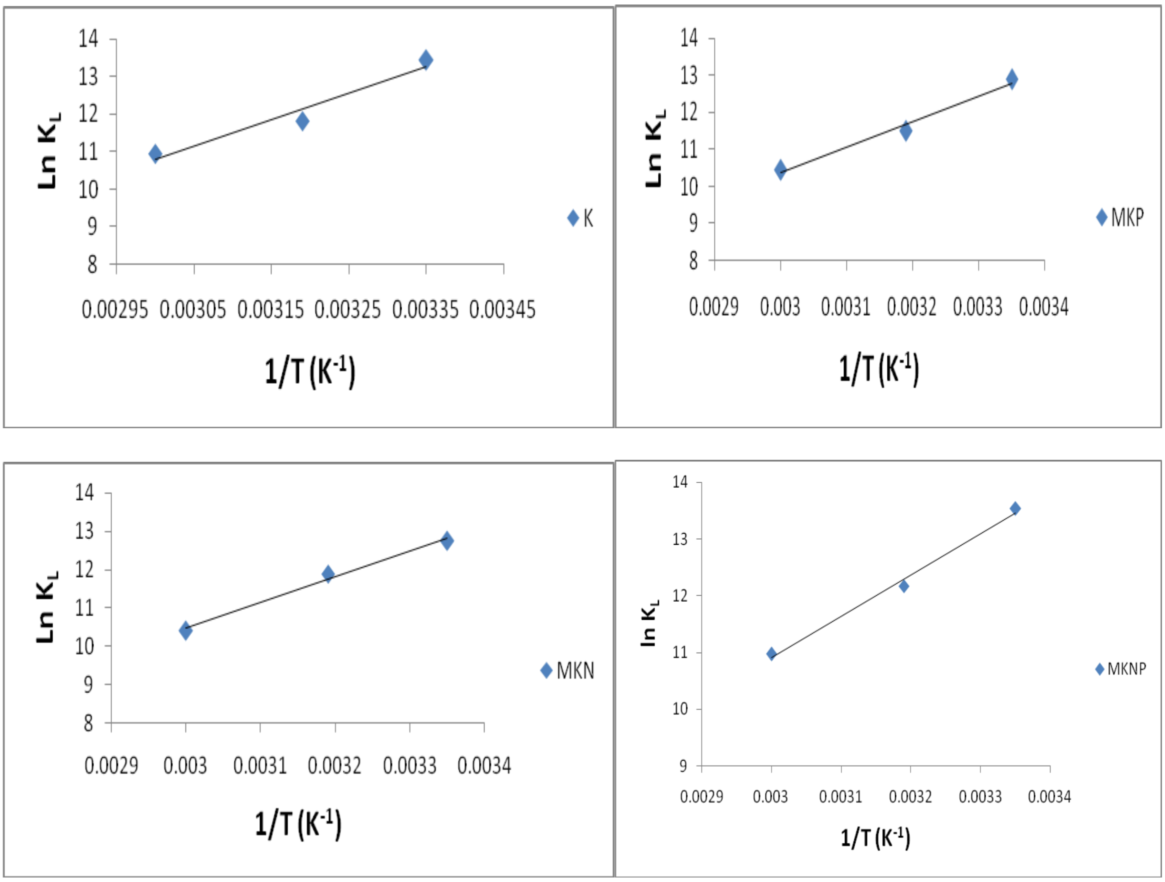


Figure (13): Vant Hoff plots for the adsorption of BBG onto kaolin and modified kaolin samples

4. CONCLUSION

Kaolin and chemically modified kaolin samples were successfully used as effective adsorbents for the removal of BBG from aqueous solutions. Acid modification with nitric acid gave the best results. It led to slight enhancement in the surface area, total pore volume, and also pore diameter of the modified samples. BET analysis showed that modification with nitric acid led to a slight increase in surface area from 102 m^2/g to 115 m^2/g. The average pore diameter enhanced from 10 to 14nm. SEM analysis represented the different characteristic features of the investigated samples and modification with nitric acid also led to the creation of pores. FTIR analysis revealed the existence of Si – O – Al bending frequencies where Al is found in octahedral coordination. XRD analysis found to contain predominatly kaolinite (55%) and quartz minerals (36%). The experimental adsorption data was fitted according to the following order: Langmuir> Halsey> Freundlich> Elovich > Temkin > Flory – Huggins > and Harkin – Jura isotherm models. Thermodynamic studies indicated that the adsorption is exothermic and spontaneous in nature.

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