Modeling of Adsorption Isotherms of Methylene Blue onto El-gash River Sand

Dr . Nabil. S. Osman
Department of Chemistry and Biology, Faculty of Education, University of Kassala.

Imad Eldeen. A. Mahajoub
Department of Chemical Engineering and Chemical Technology, Faculty of Engineering and Technology, University of Gezira.

ABSTRACT:

The El-gash river sand was analyzed for grain size, The specific surface area , The point of zero charge (pH_{PZC}), X-ray diffraction (XRD) and scanned by Electron Microscopy (SEM). The grain-size analysis of the analyzed sample revealed that it contains the fraction of (< 0.063 - >2.00 mm). The grains of the analyzed sample are Fine to medium-grained, sub rounded to sub angular grains and moderately sorted. It has been found that the point of zero charge (7.89) and the specific surface area(10.35 m^2/g). The **X-ray** diffraction analysis showed that the studied sample composes of the following minerals: quartz, albite, muscovite and anorthoclase. The Energy Dispersive X-ray Spectrum Scope(**EDX)** analysis shows that the studied contains dominantly silica and aluminum. However, the elements: iron, magnesium, sodium, calcium, potassium and manganese are occur in lesser amounts. The adsorption equilibrium isotherms of methylene blue onto El-gash river sand were studied and modeled. In order to determine the best fit isotherm, the experimental equilibrium data were analyzed using thirteen adsorption isotherm models with two-parameter equations- Langmuir and Freundlich isotherms; nine three-parameter equations - Sips, Langmuir-Freundlich and Tóth isotherms**.** The results reveal that the adsorption isotherm models fitted the experimental data in the order: Langmuir(two-parameter) > Langmuir-Freundlich = Sips(three-parameter) > Tóth(three-parameter) > Freundlich(two-parameter).

Key words: Isotherm Models , Adsorption, Adsorbent and Adsorbate.

المستخلص:

عينـة رمـل نهـر القـاش تـم تحليلهـا بواسـطة حجـم الحبيبـات، المسـاحة السـطحية النوعيـة، نقطـة شـحنة الصفـر، انحـراف الأشـعة السـينية وتـم مسـحها بواسـطة الماسـح الالكـتروني الضـوئي. تحليـل حجـم الحبيبـات للعينـة تحـت الدراسـة كشـفت بـأن العينـة تحتـوى علـى جزئيـات بـين (< 0.63- <2.00 mm). مـن ناحيـة أخـرى نجـد أن العينـة تحـت الدراسـة متوسـطة الزوايـا والكرويـة مـما يـدل عـلى أن المسـافة التـي قطعتهـا طويلـة. وجـد أن شـحنة نقطـة الصفـر(7.89) والمسـاحة السـطحية النوعيـة (10.35 m^2/g). خـلال الدراسـة للعينـة بواسـطة انحـراف الأشـعة السـينية وجـد أن الرمـل يتكـون مـن الكوارتـز، الألبيـت، المسـكوفيت والانورسـوكلايز. التحليـل بواسـطة مجـال طيـف أشـعة الطاقـة السـينية التفريقـي اظهـر أن العينـة تحـت الدراسـة تحتـوى بصـورة مهيمنـة عـلى السـليكا والالمنيـوم، عـلى أي حـال معـادن الحديـد، الماغنسـيوم، الصوديـوم، الكالسـيوم، البوتاسـيوم والمنجنيـز توجـد بصـورة قليلـة في العينـة. ايسـوثيرمات الامتـزاز عنـد الاتـزان للميثيـل الأزرق عـلى رمـل نهـر القـاش تمـت دراسـتها ونمذجتهـا. ولـكي يقـرر أفضـل ايسـوثيرم لائـق، بيانـات الاتـزان التجريبيـة حللـت باسـتعمال نمـاذج ايسـوثيرم الامتـزاز مـع معـادلات ذات معامـلات ثنائيـة(لانكمـير وفرينـدلـش) ومعـادلات ذات معامـلات ثلاثيـة(سـيبس، لانكمـير -فرينـدلـش وتـوث). تكشـف النتائـج بـأن نمـاذج ايسـوثيرم الامتـزاز توافقـت مـع البيانـات التجريبيـة كـما يـلي:

لانكمير(ثنـائى المعامـل) > لانكمـير- فرينـدلـش (ثـلاثى المعامـل)= سـيبس (ثـلاثى المعامـل)> تـوث (ثـلاثى المعامـل) > فرينـدلش(ثنـائى المعامـل).

كلمات مفتاحيه: نماذج الايسوثيرمات ، الامتزاز، الماز والممتز.

INTRODUCTION

Among the different pollutants of aquatic ecosystems, dyes are a large and important group of industrial chemicals for which world production in 1978 was estimated at 640,000 tons [1]. Most of this quantity was used in the textile industry and the dyes in use include many different compounds and their environmental behavior is largely unknown[2] . Interest in the environmental behavior of dyes is prompted primarily by concern over their possible toxicity and carcinogenicity, heightened by the fact that many dyes formerly were made of known carcinogens such as benzidine, which may be reformed as a result of metabolism [2]. Disperse dyes have been shown to have high partition coefficients and solubility, suggesting significant potential for bio- concentration [3]. Dye toxicity is not well defined in plant effluents and their long-term effects on animal and human health are not documented, with an exception of a study by Sturm and co-workers [4]. Most dyestuffs are designed to be resistant to environmental conditions like light, effects of pH and microbial attack[5]. Among the methods employed are the adsorption onto sludge of waste water treatment plant, as well as other physicochemical techniques as coagulation, flocculation, ozonation, reverse osmosis and adsorption on activated carbon, manganese oxide, silica gel and clays[6-9]. The purpose of this work is the study of the removal of selected methylene blue dyes from water, by adsorption on El-gash River Sand.

MATERIALS and METHODS

Preparation of Adsorbent

Sand used in this study was obtained from the bottom sediment of El-gash river Kassala State, Sudan. The sample was collected from 20 centimeter deep using stainless steel scoop [10]. The Sand sample was left overnight to dry at room temperature. Dried sample was sieved through different size . The sample was heated in an oven at temperature of 110^{o} C and then kept in the desiccator.

Preparation of Adsorbate

The use of methylene blue (MB) ($C_{16}H_{18}ClN_3S$ $3.H_2O$) was purchased from HIMEDIA and molecular weight of 373.9. A methylene blue stock solution was prepared by dissolving (1g) of MB in distilled water (1 L).

Material Characterization

Grain Size Analysis

The sample was subjected to mechanical dry sieving analysis.

During the sieve analysis, 100 gm of sample was weighted. This weighted sample was analyzed by OCTAGON digital (00363) for fifteen minutes under amplitude 4 and the instrumental shaking was kept intermittent. Then each size fraction has been collected from the sieves into porcelain dishes by the aid of brush and Ultrasonic. The fractions weights were recorde[11].

X-Ray Diffraction (XRD) Analysis

The sand was characterized by diffraction of X rays (XRD), using the Philips X'Pert 1 X-ray Diffract meter type 7602 EA Almelo. X-ray diffraction analysis was carried out in order to identify and semi-quantitatively deduce the percentages of the different minerals that are present in the studied sample[11].

Scanning Electron Microscopic (SEM)Analysis

The Scanning electron microscopy analysis was carried out on the analyzed sample. The sample fixed on standard aluminum SEM stub using sputter aluminum tape. The SEM analysis involved a detailed investigation and description for the sample material with special focus on the grain surfaces and textures[11].

The Specific Surface Area

The specific surface area of El-gash river sand was determined by the method of methylene blue (MB) described by Hang and Brindly [12]. The adsorption capacity of MB was obtained from batch adsorption experiments. A series of 50mL bottles were employed. Each bottle was filled with 100 mL of MB solution of varying concentrations (1-8 mg/L standards) and 0.05 g of El-gash river sand. The stoppered bottles were shaken at 30^0C and 150 rpm for 48 h. A 10.0 mL portion of each solution was withdrawn after 48 h and centrifuged. The MB concentrations were determined spectrophotometrically using UV–vis spectrophotometer (JENWAY 6305) at λ_{max} = 665 nm.

The Point of Zero Charge (pH_{PZC})

The method proposed by[13] was followed. The point of zero charge was determined from acid-base titration. For this, fifty ml of 0.01 M sodium chloride solution were prepared in six volumetric flasks. Their pH was adjusted with addition solution of sodium hydroxide or hydrochloric acid. When the pH value was constant, 0.15 g of El-gash river sand sample was added to each flask and shaken for 24 h. The mixture was filtrated and the electrode of the pH meter was inserted into the six solutions and the pH was read and recorded.

Theory of Adsorption Models

The successful representation of the dynamic adsorptive separation of solute from solution onto an adsorbent depends upon a good description of the equilibrium separation between the two phases. Adsorption equilibrium is established when the amount of solute being adsorbed onto the adsorbent is equal to the amount being desorbed. At this point, the equilibrium solution concentration remains constant. By plotting solid phase concentration against liquid phase concentration graphically it is possible to depict the equilibrium adsorption isotherm. There are many theories relating to adsorption equilibrium.

Two- Parameter of Adsorption Models

A brief review of two parameter isotherm models used in the present study can be presented below:

Langmuir Model

Langmuir adsorption which was primarily designed to describe gas-solid phase adsorption is also used to quantify and contrast the adsorptive capacity of various adsorbents[14]. The Langmuir isotherm theory assumes monolayer coverage of adsorbate over a homogenous adsorbent surface[15]. Langmuir isotherm accounts for the surface coverage by balancing the relative rates of adsorption and desorption (dynamic equilibrium). Therefore, at equilibrium, a saturation point is reached where no further adsorption can occur. Sorption is assumed to take place at specific homogeneous sites within the adsorbent. Once a dye molecule occupies a site, no further adsorption can take place at that site. The Langmuir equation can be written in the following non-linear form[16]:

$$q_e = \frac{Q_m k_L C_e}{1+k_L C_e} ....(1)$$

Where Q_m and K_L are the Langmuir isotherm constants; C_e and q_e are the liquid phase concentration and solid phase concentration of adsorbate at equilibrium. Hence by plotting q_e against C_e it is possible to obtain the value of K_L , and The theoretical monolayer capacity Q_m. The Langmuir equation is applicable to homogeneous sorption where the sorption of each molecule has equal sorption activation energy.

Freundlich Model

The Freundlich expression (Eq. (2)) is an exponential equation and therefore, assumes that as the adsorbate concentration increases so too does the concentration of adsorbate on the adsorbent surface. Theoretically, using this expression, an infinite amount of adsorption can occur [17].

$$q_e = k_f C_e^{1/n_f} ....(2)$$

In this equation K_f and n_f are the Freundlich constants. This expression is characterized by the heterogeneity factor, n_f , and so the Freundlich isotherm may be used to describe heterogeneous systems [18].The Freundlich equation agrees well with the Langmuir over moderate concentration ranges but, unlike the Langmuir expression, it does not reduce to the linear isotherm (Henry’s Law) at low surface coverage. Both these theories suffer from the disadvantage that equilibrium data over a wide concentration range cannot be fitted with a single set of constants[19].

Three- Parameter of Adsorption Models

Sips Model

Recognizing the problem of the continuing increase in the adsorbed amount with an increase in concentration in the Freundlich equation, Sips proposed an equation similar in form to the Freundlich equation, but it has a finite limit when the concentration is sufficiently high and it is given the following general expression

$$q_e = \frac{q_{m_s} K_s C_e^{m_s}}{1 + K_s C_e^{m_s}} \quad ....(3)$$

Where q_e is the adsorbed amount at equilibrium (mg/g), C_e the equilibrium concentration of the adsorbate (mg/L), q_{ms} the Sips maximum adsorption capacity (mg/g), K_s the Sips equilibrium constant (L/mg), and m_s is the Sips model exponent[20].

Langmuir-Freundlich Model

The Langmuir- Freundlich equation is given by(9):

$$q_e = \frac{q_{m_{LF}} (K_E\ C_e)^{m_E}}{1 + (K_E\ C_e)^{m_E}} \quad ....(4)$$

Where q_e is the adsorbed amount at equilibrium (mg/g), q_{mLF} the Langmuir- Freundlich maximum adsorption capacity (mg/g), C_e the adsorbate equilibrium concentration (mg/L), K_{LF} the equilibrium constant for a heterogeneous solid, and m_{LF} is the heterogeneous parameter, lies between 0 and 1.

Toth Model

The Toth isotherm is another empirical modification of the Langmuir equation with the aim of reducing the error between experimental data and predicted value of equilibrium data[21]. This model is most useful in describing heterogeneous adsorption systems which satisfy both low and high end boundary of adsorbate concentration[22].The Toth isotherm model is expressed as follows(22):

$$q_e = \frac{q_{m_T} C_e}{\left(1/K_T + C_e^{m_T}\right)^{1/m_T}} \text{..............(5)}$$

Where q_e is the adsorbed amount at equilibrium (mg/g), C_e the equilibrium concentration of adsorbate(mg/L), the Toth maximum adsorption capacity(mg/g), K_T is Toth isotherm constant (mg/g) and m_T is Toth isotherm constant (mg/g). It is clear that when m_T = 1, this equation reduces to Langmuir isotherm equation. Therefore the parameter m_T characterizes the heterogeneity of the adsorption system[21] and if it deviates further away from unity (1), then the system is said to be heterogeneous. This isotherm model has been applied for the modeling of several multilayer and heterogeneous adsorption systems(23).

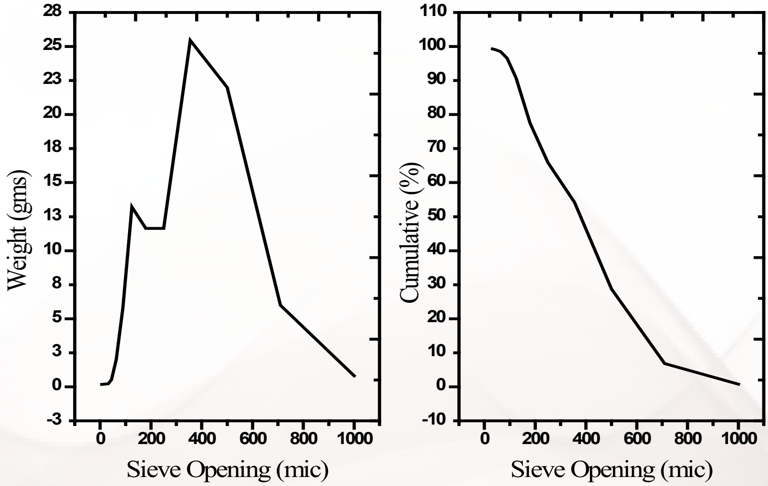
RESULTS and DISCUSSION

Grain Size Analysis Result

The objective of this analysis was carried out in order to identify the potential sand classes, its grain size parameters as well as the texture maturity of the sample. The grain-size analysis of the analyzed sample revealed that it contains the fraction of (< 0.063 - >2.00 mm). The dominant granulometric main class of the studied sample is medium sand grain-size fraction, while the clay and silt fractions are occur in minor amount. However, the pebble and the granule classes are relatively absent. Furthermore, the grains of the analyzed sample are Fine to medium-grained, sub rounded to sub angular grains and moderately sorted[11]. The result show in Table (1).

Table (1).: Grain size analysis result .

Size Grade	Sieve Opening(mic)	Phi (Ø)	Weight (gms.)	Weight %	Cumulative %
V.C Sand	1000	0.00	0.80	0.80	0.80
C. Sand	710	0.50	6.00	6.00	6.80
	500	1.00	21.98	21.98	28.78
M. Sand	355	1.50	25.45	25.45	54.23
	250	2.00	11.64	11.64	65.87
F. Sand	180	2.50	11.63	11.63	77.50
	125	3.00	13.22	13.22	90.72
V.F. Sand	90	3.50	5.83	5.83	96.55
	63	4.00	1.99	1.99	98.54
Silt	45	4.50	0.53	0.53	99.07
	32	4.75	0.22	0.22	99.29
Pan	10 <32	6.50	0.17	0.17	99.46
Sieve Loss			0.54	0.54	100.00
Total Weight after Sieve			39.90		



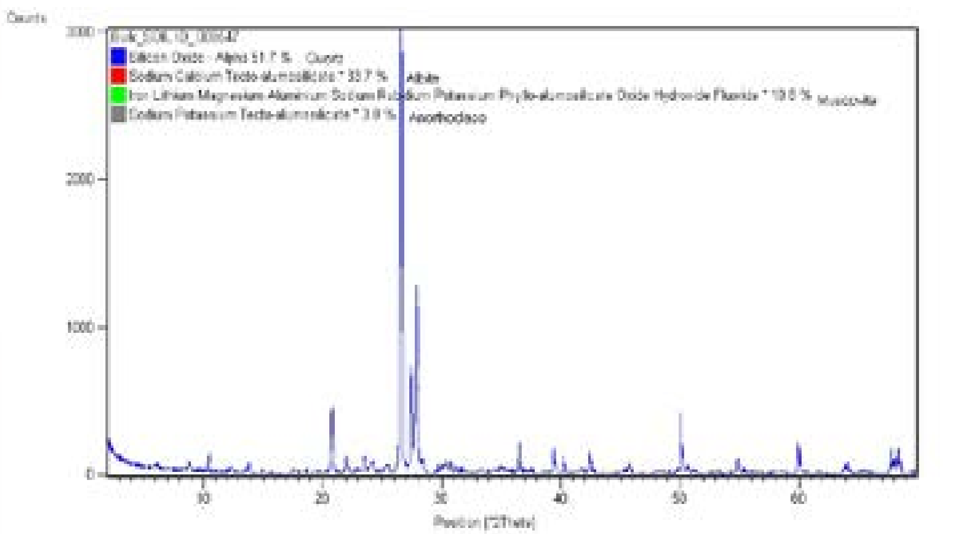
Figure(1): The sieve opening vs. weight and Cumulative for sand sample .

X-Ray Diffraction Analysis Result

The X-ray diffraction analysis showed that the studied sample composes of the following minerals: quartz, albite, muscovite and anorthoclase[11]. The result present in Table 2 and Figure(2) .

Table 2: The minerals percentages results using X-ray diffraction analysis.

Sample Type	Mineral Name	Percentages (%)
Soil	Quartz	51.7
	Albite	33.7
	Muscovite	10.8
	Anorthoclase	3.80



Figure(2): The X - ray diffraction of the sand sample.

SEM Analysis Result

The studied sample under the SEM revealed that the grains surfaces are moderately hatched but the spherecity of the grains is ellipsoid in shape. The amount of the sand ratio is much greater than the mud ratio, which means the textural maturity is very high. The dispersive energy spectrum (EDX) analysis shows that the studied contains dominantly silica and aluminum. However, the elements: iron, magnesium, sodium, calcium, potassium and manganese are occur in lesser amounts[11]. The result present in Figure(3 and 4) .

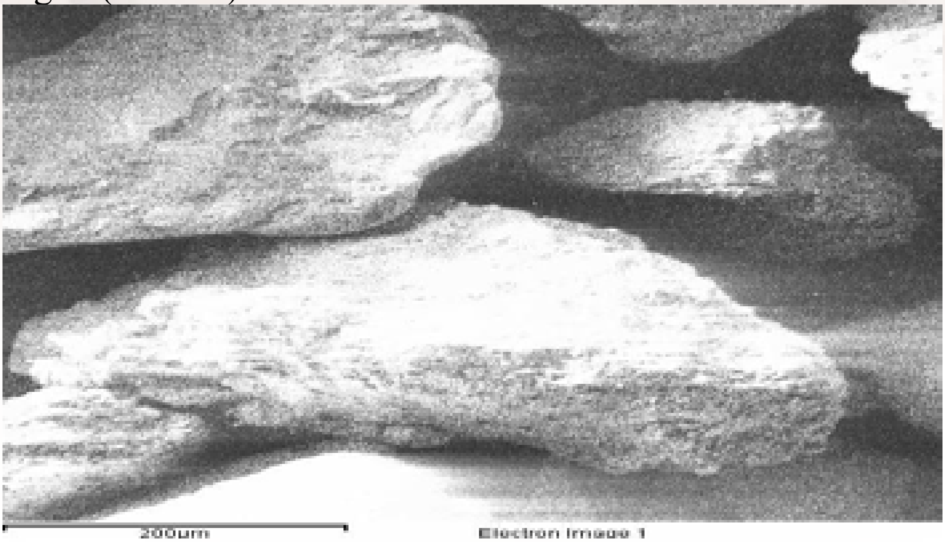


Figure (3): The SEM micrograph of the sand particles.

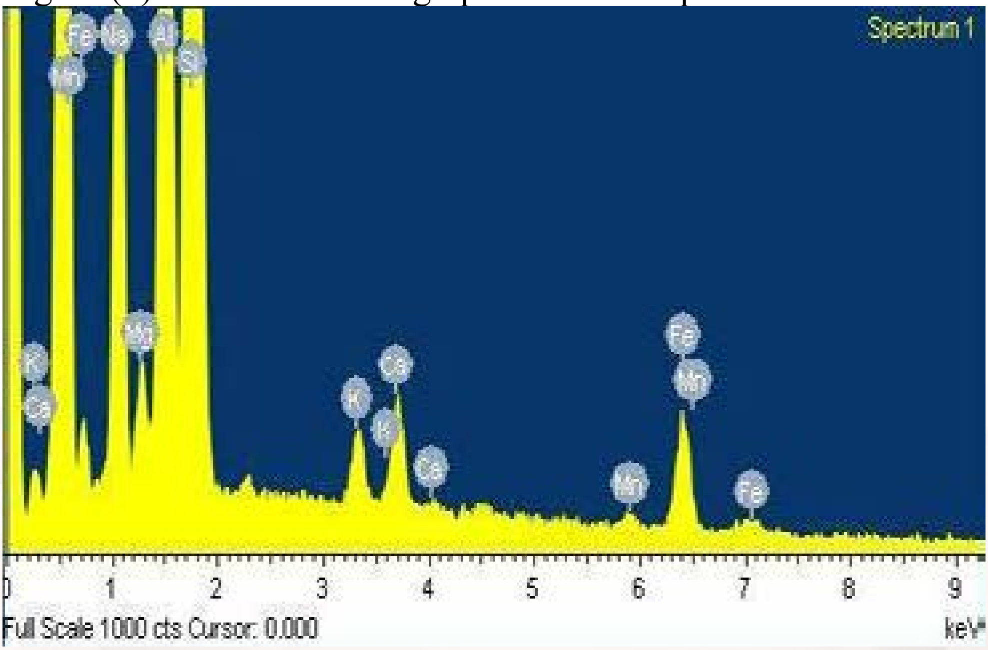


Figure (4): The EDX of sand spectroscopy.

The Specific Surface Area(SSA)

The adsorption data of MB onto El-gash river sand (Fig. 5). Was analyzed according to Langmuir equation (Eq. (6)).

$$q_e = \frac{Q_m k_L C_e}{1 + k_L C_e} \text{...............} (6)$$

Where q_e is the amount of MB adsorbed (mg MB/g El-gash river sand), Q_m is the monolayer adsorption capacity (mg MB/g El-gash river sand), K_L is the affinity constant (L/mg MB), and C_e is the equilibrium solution concentration of MB (mg/L). The value of Q_m obtained was 4.942 mg MB/g El-gash river sand.

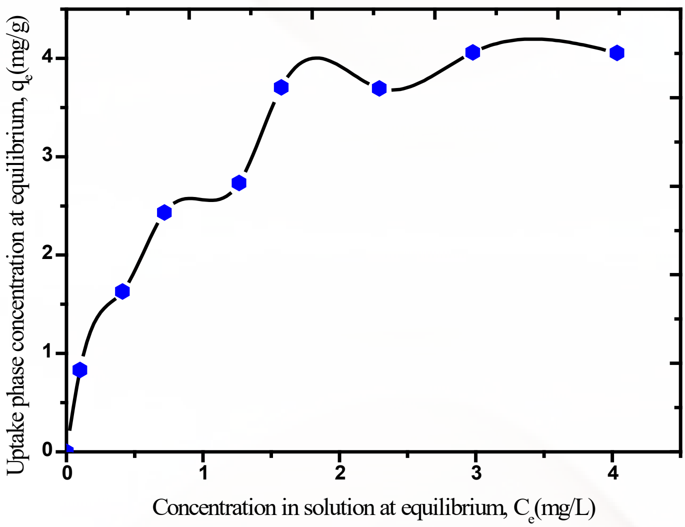


Fig. 5. Adsorption isotherm for methylene blue (MB) onto El-gash river sand.

Depending on this value the specific surface area (S) of El-gash river sand can be calculated from Eq. (7) [12, 24].

$$S = Q_m \times CSA \times N \text{...............} (7)$$

Where CSA is the cross-sectional area occupied by MB molecule ($130 A^2$) and N is the Avogadro's number (mol^{-1}). The specific surface area of El-gash river sand was found to be 10.35 m^2/g. It is worth to mention that MB molecules occur nearly completely in the monomeric form in solutions of concentrations in the range(1-8 mg/L) used in the present study(24).

The Point of Zero Charge (pH_{PZC})

The point of zero charge pHpzc is important guides to these interfacial properties. The techniques for the determination of pHpzc are founded on the assumption that protons, H^+, and hydroxyl groups, OH^-, are potential determining ion. Silica and other powder in an aqueous medium adsorb H^+, OH^- ions. The pH at which the surface has zero net charge, Known as pHpzc is characteristic of amphoteric surface an determined by the type of surface sites on solid and their structures[25]. The result is shown in Figure(6).

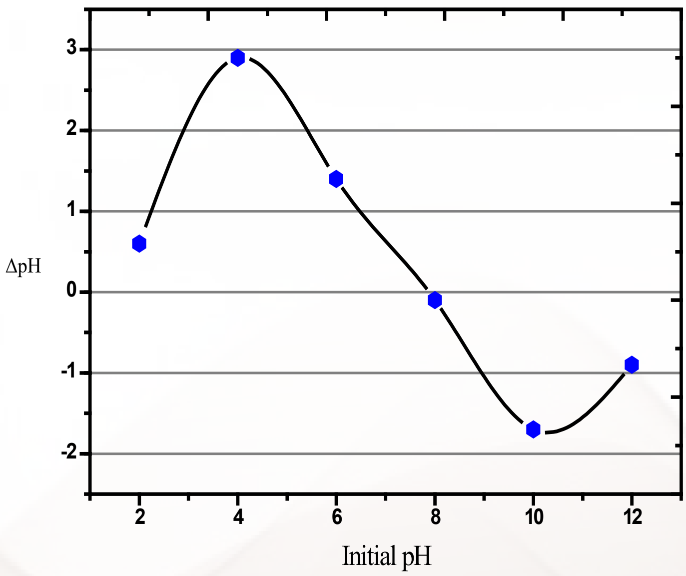


Figure (6): The ΔpH vs. Initial pH.

For values of pH < PZC, the El-gash river sand surface has been positively charged. At pH > PZC the El-gash River Sand surface has been negatively charged. It was shown that the sample particles shift the net surface charge of El-gash river sand from negative to positive and the point of zero charge (PZC) of tested sample equal 7.89. The pH at which the adsorption densities of potential-determining cations and anions are the same is known as the point of zero charge of the particles. The particle surface is negatively charged at pH values above the pH_{pzc}, and positively charged when the pH is below the pH_{pzc}. The common plateau obtained at a pH value of 7.4±0.1[26]. Milonjić et al (2007) reported that the point of zero charge of the same silica samples ranging from 3.8 to 7.1[25].

Equilibrium Isotherms Modeling

The adsorption equilibrium data for methylene Blue onto El-gash river sand were analyzed by non-linear curve fitting analysis, using OriginPro8.5 software, to fit the two and three parameter isotherm model. The experimental values of q_e and C_e are initially treated with the models in order to determine the equations parameters and the isotherms are reconstituted using the determined values. The isotherm curves showed the superposition of experimental results(lines) and the theoretical calculated points(points). The correlation coefficients (R^2) showed the fit between experimental data and isotherm equations.

Two-parameter of Adsorption Models

Langmuir Model

The isotherm data has been fitted using non-linear Langmuir equation and is plotted between q_e versus C_e which is shown in Figure (7). The Langmuir constant q_m which is measure of the monolayer adsorption capacity of El-gash river sand, is obtained as ***4.942 mg/g***. The Langmuir constant k_L , which denotes adsorption energy, is found to be ***1.327 L/mg***. The high value of coefficient of determination (***R^2 = 0.957***) obtained indicates a good agreement between the experimental values and isotherm parameters and also confirms the monolayer adsorption of methylene blue onto El-gash river sand surface.

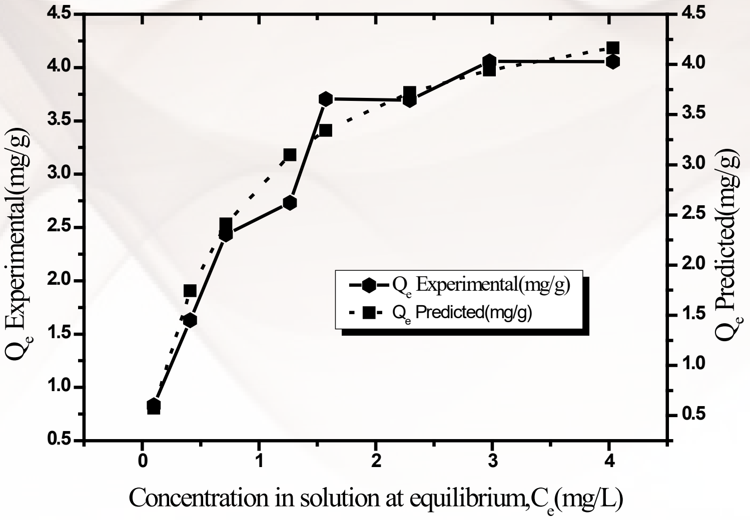


Fig.7: Comparison of experimental and predicted adsorption isotherms of methylene blue onto El-gash river sand according to Langmuir model.

Freundlich Model

The Freundlich constant, k_f and n_f are obtained by plotting the graph between q_e versus C_e as shown in figure (8). The values of k_f and n_f are ***2.622*** and ***2.640*** respectively. It is found that the coefficient of determination obtained from the Freundlich isotherm model for El-gash river sand is($\boldsymbol{R^2 = 0.921}$) which is lower than that for Langmuir isotherm model as given in Table (1). Freundlich isotherm model is widely used but does not provide the information on the monolayer adsorption capacity. The obtained result indicates that the equilibrium data is not fitted well with the Freundlich isotherm model.

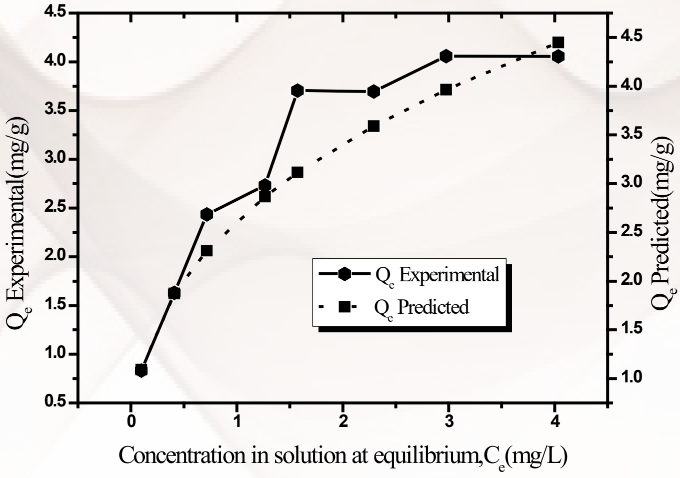


Fig.8: Comparison of experimental and predicted adsorption isotherms of methylene blue onto El-gash river sand according to Freundlich model.

Three-parameter of Adsorption Models

The abilities of the three-parameter equation Langmuir-Freundlich, Fritz- Schlunder, Sips and Tóth isotherms, to model the equilibrium adsorption data were examined. Table (1) shows the isotherms parameters obtained using the non-linear fitting analysis. Among the tested three- parameter equation, the better and perfect representation of the experimental results of the adsorption isotherms is obtained using the Langmuir-Freundlich model (Fg.9). According to Table (1), the coefficients of correlation are very good($R^2 = 0.951$). The values of the maximum adsorption capacity obtained using the Langmuir-Freundlich equation are higher than calculated by the Langmuir model and lower than the theoretical value(***5.405mg/g***). This indicates that, according Langmuir-Freundlich isotherm, methylene blue is not adsorbed in flat on the adsorbent surface.

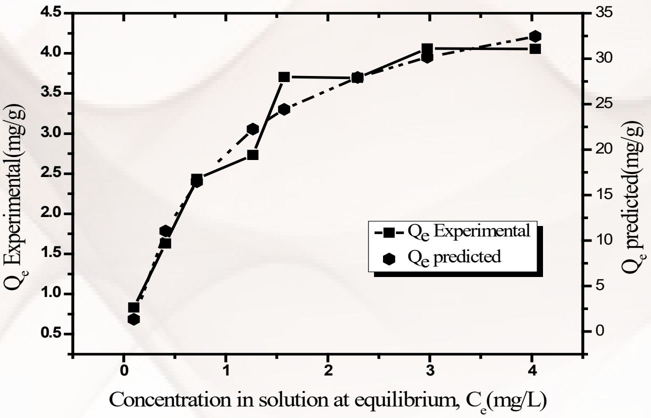


Fig.9: Comparison of experimental and predicted adsorption isotherms of methylene blue onto El-gash river sand according to Langmuir-Freundlich model.

The prediction of adsorption isotherms of methylene blue onto El-gash river sand by the Sips model is shown on Fig.10. The Sips equation fits adequately the experimental results Table (1), the Sips equation seems slightly better than that of Langmuir-Freundlich. The maximum adsorption capacities is identical to the obtained using the Langmuir-Freundlich isotherm. The parameter K_S and m_S change in the same manner as the constant k_{LF} and m_{LF} of the equation of Langmuir-Freundlich.

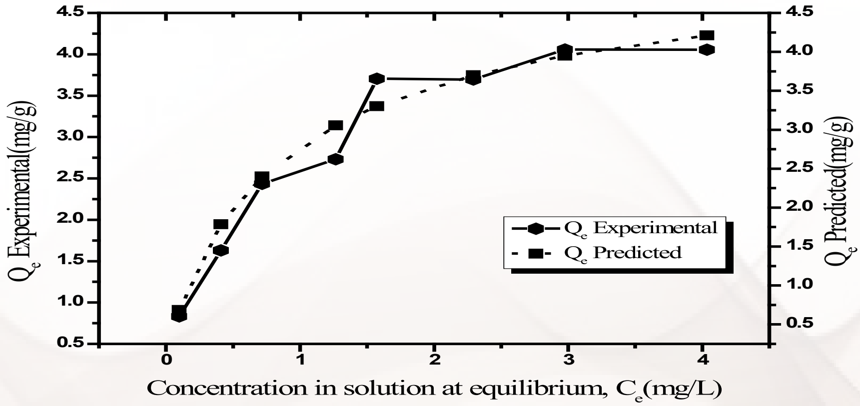


Fig10: Comparison of experimental and predicted adsorption isotherms of methylene blue onto El-gash river sand according to Sips model.

The Tóth model correctly simulated the adsorption isotherm of the studied methylene blue compound(Fig.11). The coefficient of correlation are good (***R^2 = 0.950***) for tested molecule. On the basis of the coefficient of correlation value (Table 1), the Langmuir-Freundlich and Sips equations seems slightly preferably than that of the Tóth isotherm. The adsorption maximum capacities determined using the Tóth model are higher than those of Langmuir, Langmuir-Freundlich and Sips. The maximum adsorption capacities is higher than the theoretical value (***5.452 mg/g***). This indicate that, according to Tóth model is adsorbed flat on the El-gash river sand surface.

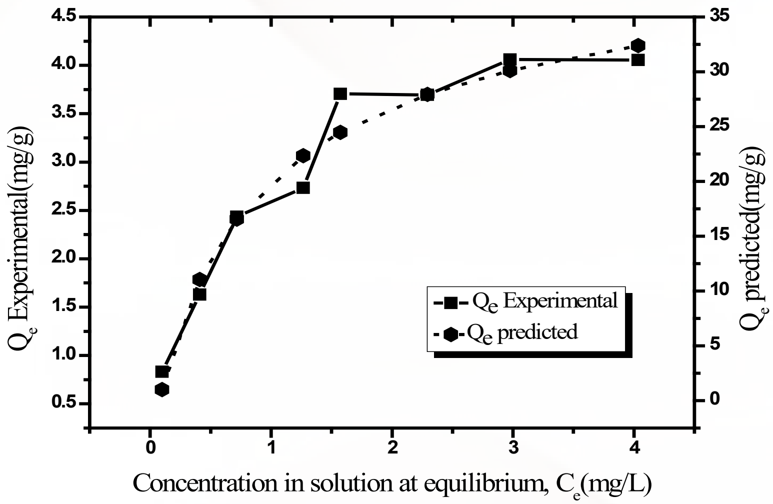


Fig.11: Comparison of experimental and predicted adsorption isotherms of methylene blue onto El-gash river sand according to Toth model.

The results reveal that the adsorption isotherm models fitted the experimental data in the order: Langmuir(two-parameter) > Langmuir-Freundlich = Sips(three-parameter) > Tóth(three-parameter) > Freundlich(two-parameter).

Table(1):Values of the parameters of the two-parameter models, three-parameter models and correlation coefficients.

Langmuir model			
Q_m mg/g	K_L L/mg		R^2
4.942	**1.327**		**0.957**
Freundlich model			
K_f	n_f		R^2
2.622	**2.640**		**0.921**
Sips model			
q_{ms} mg/g	K_s L/mg	m_s	R^2
5.403	**1.063**	**0.861**	**0.951**
Langmuir-Freundlich model			
q_{mLF} mg/g	K_{LF}	m_{LF}	R^2
5.403	**1.073**	**0.861**	**0.951**
Tóth model			
q_{mT} mg/g	K_T L/mg	m_T	R^2
5.459	**1.410**	**0.800**	**0.950**

CONCLUSION

The petrographic the scanning electron microscope analyses beside the grain size and the X-ray diffraction analyses showed that: the source rock origin of the analyzed sample. Is mainly come out from acidic nature rocks (granite and/or granodioritic gneiss) with lesser contribution from basic rocks (basalt and/or gabbro). Since the studied sample characterized by high sand/mud ratio, dominant sub rounded to sub angular grains and moderately sorted, this sediment was subjected relatively to strong reworking effects, which enables the detrital constituents to be recycled and transported for relatively long distance. The results reveal that the adsorption isotherm models fitted the experimental data in the order: Langmuir(two-parameter) > Langmuir-Freundlich = Sips(-three-parameter) > Tóth(three-parameter) > Freundlich(two-parameter).

REFERENCES

(1) Clarke, E.A. and R. Anliker, *Organic dyes and pigments. In: The Handbook of Environmental Chemistry- . Anthropogenic Compounds, Hutzinger*, O. (Ed.), Editor 1980, Springer-Verlag: Heidelberg. p. 181-215.

(2) Baughman, G. and T.A. Perenich, *Fate of dyes in aqueous systems: Solubility and partitioning of some hydrophobic dyes and related compounds.* Environ. Toxicol. Chem, 1988. **7**: p. 183-199.

(3) Anliker, R., E.A. Clarke, and P. Moser, *Use of the partition coefficient as an indicator of bioaccumulation tendency of dyestuffs in fish.* Chemosphere, 1981. **10**: p. 263-274.

(4) Sturm, K., E. Williams, and K.J. Macek, *Fluorescent whitening agents Acute fish toxicity sand accumulation studies, Water Resources.* 1975. **9**: p. 211-219.

(5) Pagga, U.M. and K. Taeger, *Development of a method for adsorption of dyestuffs on activated sludge.* Water Resources, 1994. **28**: p. 1051-1057.

(6) Davis, L. and C. Randal, *Development of color removal potential in organisms treating pulp and paper wastewaters.* J. WPCF, 1978. **50**: p. 382-386.

(7) Pollock, M., *Neutralizing dye-house wastes with flue gases and decolorizing with fly ash.* American Dyestuff Reporter, 1973. **62**: p. 21-23.

(8) Arvanitoyannis, I., I. Eleftheriadis, and E. Kavlentis, *Treatment of dye containing effluents with different bentonites.* Chemosphere, 1987. **16**: p. 2523-2529.

(9) Arvanitoyannis, I., I. Eleftheriadis, and E. Tsatsaroni, *Influence of pH on adsorption of dye-containing effluents with different bentonites.* Chemosphere, 1989. **18**: p. 1707-1711.

(10) Page, A.L., R.H. Miller, and D.R. Kuney, *Methods of soil analysis part 1&11*, 1982, Soil science of Am. Inc: Madison, USA. p. part 1,199-223, 581-593; part11, 383-409,493-541pp.

(11) Sudanese, P.C., C.P. Laboratories, and *Petrographical, Grain Size, X-Ray Diffraction and Scanning Electron Microscopic Analyses on One Soil Sample*, 2009.

(12) Hang, P.T. and G.W. Brindly, *Methylene blue adsorption by clay minerals. Determination of surface areas and cation exchange capacities.* Clays Clay Miner, 1970. **18**: p. 203.

(13) Rivera-Utrilla, J., et al., *Chem. Technol. Biottechnol.* 2001: p. 76-1209.

(14) Elmorsi, T.M., *Equilibrium isotherms and kinetic studies of removal of methylene blue dye by adsorption onto miswak leaves as a natural adsorbent.* Journal of Environmental Protection, 2011. **2, no. 6**: p. 817–827.

(15) Langmuir, I., *The adsorption of gases on plane surface of glass, mica and platinum.* J. Am. Chem. Soc, 1918. **40**: p. 1361–1403.

(16) browski, A.D., *Adsorption—from theory to practice.* Advances in Colloid and Interface Science, 2001. **93, no. 1–3**: p. 135–224.

(17) Freundlich, H., *Uber Die Adsorption in hosungen.* Z. Phys. Chem, 1906. **57**: p. 387–470.

(18) Boparai, H.K., M. Joseph, and D.M. O'Carroll, *Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles.* Journal of Hazardous Materials, 2011. **186, no. 1**: p. 458–465.

(19) McKay, G., *Kinetics of colour removal from effluent using activated carbon.* JSDC, 1980. **96**: p. 576–579.

(20) Jeppu, G.P. and T.P. Clement, *A modified Langmuir-Freundlich isotherm model for simulating pH-dependent adsorption effects.* Journal of Contaminant Hydrology, 2012. **129-130**: p. 46–53

(21) Behbahani, T.J. and Z. Jafari Behbahani, *A new study on asphaltene adsorption in porous media.* Petroleum and Coal, 2014. **56, no. 5**: p. 459–466.

(22) Padder, M.S. and C.B. C.Majunder, *Studies on Removal ofAs(II) and S(V) onto GAC/MnFe, 804 Composite.* Isotherm-Studies andmError Analysis, 2012.

(23) Benzaoui, T., A. Selatnia , and D. Djabali, *Adsorption of copper (II) ions from aqueous solution using bottom ash of expired drugs incineration.* Adsorption Science and Technology, 2017: p. 1–16.

(24) Inel, O. and F. Tumsek, *The measurement of surface areas of some silicates by solution adsorption.* Turk. J. Chem, 2000. **24**: p. 9–19.

(25) Milonjić, S.K., L.S. Ćerović, and S.Z. Ćokeša, *The influence of cationic impurities in silica on its crystallization and point of zero charge.* Journal of Colloid and Interface Science, 2007. **309**: p. 155- 159.

(26) Lazarević, S., et al., *The influence of cationic impurities in silica on its crystallization and point of zero charge.* Journal of Colloid and Interface Science, 2007. **309**: p. 155-159.