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Kinetics, Isotherm and Optimum Condition for the Adsorption of Methyl Red Dye Using Hydroxyapatite

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ABSTRACT

The aim of the experiment is to remove dyes from wastewater using adsorption technique. The hydroxyapatite was used as an adsorbent to remove methyl red dye. The adsorption process was carried out with four different experiments. The first one is changing the contact time, and the optimum contact time was found to be 90 minutes with a 97 percent removal. The second experiment was carried away by changing the pH of the medium and using the optimum contact time obtained from the previous experiment. The optimum pH in the second experiment was found to be 4 with a 91.6 percent removal. The third interpretation was analysed by changing the initial concentration of the dye and using the optimum contact time and pH obtained from the two previous experiments. The optimum initial concentration of the dye in the third experiment was found to be 0.1 ppm with a 94.6 percent removal. Finally, the fourth analysis by using the optimum time, pH and initial concentration obtained from the three previous experiments, but the adsorbent dose was changing. It was found that the optimum adsorbent dose was found to be 2 g/l with 94.6% percent removal. According to the two parameter isotherms, the adsorption process followed Freundlich isotherm model, and Halsey isotherm as they had the higher R2 values, which shows that the adsorbent surface is heterogenous. The kinetics of the adsorption process was found to be pseudo second order. The mechanism of the adsorption process was studied by intraparticle diffusion and which indicated the ionic state of the dye.

Key words: Adsorption, pH, Wastewater treatment, Freundlich isotherm

1. INTRODUCTION

Polluted water is dangerous on the public health, food, habitats as it contains toxic materials. For instance, untreated domestic wastewater contains organics, nutrients, and pathogens. However, the untreated industrial wastewater contains hazardous substance like heavy metals. Polluted wastewater causes major damage on the environment by spreading diseases and illness. Domestic wastewater composes mainly of human faece and urine, which their organic fraction composes of proteins, carbohydrates, and fats. These compounds are nutrient to bacteria and microorganism. The majorly of these bacteria are dangerous on human health as it can cause cancer and even death. On the other hand, the industries like textile, paint, dyestuff discharge toxic, mutagenic, and non-biodegradable wastewater. The estimated discharge of dyes from the textile industries only is 280.000 tons per year.

The direct discharge to the environment of the industrial wastewater cause a serious damage to ecosystem, and that is why wastewater must be treated carefully [1]-[4].

Dyes are organic compounds that are extracted from plants or they can be produced chemically. Unlike paints, dyes do not build up on the surface of the material, instant they are absorbed into the pores of the material. This phenomenon occurs because of two reasons, the first reason is the small size of the dye molecules that is smaller than the pores of most materials. The second reason is the force of attraction that held the dyes into the pores of the material (the affinity of the dye to the material being coloured) [5]-[9].

Over the years, scientists were interested in the adsorption phenomena as it has many important applications. Its importance in the biological and the environmental protection can never be doubt. Adsorption is widely used in the purification of water, air, soil, and sewages because of its superior results among the other purification techniques. Adsorption may be defined as the accumulation of any substance giving higher concentration on the surface of another substance compared to the concentration of the bulk. For instance, when a solid substance is exposed to a gas or a liquid, the molecules of the gas or the liquid accumulate on the surface of the solid substance. The gas or the liquid accumulated on the surface is called adsorbate, however, the solid where the adsorption takes place on its surface is called adsorbents [10]. This process can be done between liquid-gas, liquid-liquid, solid-liquid, and solid-gas. On a large industrial scale, the adsorption deals with mainly the solid-gas, and solid-liquid interfaces. Commercial adsorbents must be highly porous, with high abrasion resistance and high thermal stability. The pores surface area is usually in the range of 100 to 1200 m^2/g, the large surface area allows a large adsorption capacity relative to the weight of the adsorbent. It is preferred that

The pores of the adsorbent have a distinct structure to enable fast transport of gaseous substance. These porous structures of the adsorbents are important as they attract and hold organic molecules and certain metals and inorganic molecules (pollutants). The adsorption phenomena happen when the pollutants have low solubility in the water, or the pollutants have greater affinity to the adsorbent than for the water [11]-[13].

The hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) is one of the most studied material to remove dyes, fluorides, heavy metals and toxic traces like lead, cobalt, zinc, cadmium, manganese, mercury, and iron from polluted soils [14], [15]. HAp is an inorganic, safe biostable, biocompatible and non-toxic material that has a similar structure to the inorganic components of the bone. Consequently, HAp is used in artificial bone joining, dental treatment and drug delivery system as a biomedical application. Furthermore, HAp has a high sorption capacity, which makes it a very efficient adsorbent for proteins, heavy metals, and dyes separation. Also, HAp is stable under different values of pH and temperature. Its properties also include low degree of solubility in water, chemical stability, low cost, and availability [16]. These properties depend mainly on HAp morphology, surface charge and crystallinity. Therefore, the recent studies are interested in enhancing these properties by developing the HAp nanostructure to increase the efficiency of the adsorption, to remove a wide variety of dyes and heavy metals. However, the HAp has some limitations that limits its use in various application, these limitations are unstable mechanical properties and brittleness [17]-[19]. To overcome these limitations, polymeric material must be combined with the HAp to enhance its poor mechanical properties and to get better results like, improved stiffness, strength, and modulus [3].

The research was divided into four experiment, first is changing the contact time. The second experiment was carried away by changing the pH of the medium. The third interpretation was analysed by changing the initial concentration of the dye. Finally, the fourth analysis, is changing the adsorbent dose, and through all these experiments, the optimum percent removal was determined at certain conditions. The spectrophotometer was used to determine the absorbance of each sample. Adsorption isotherm models, kinetics and mechanism were analysed throughout the experiment.

2.EXPERIMENTAL

2.1 Time Optimization

In the first experiment, six samples were prepared with 0.16 g of adsorbent dosages, 0.5 mg/l of dye concentration, and pH equal to 4. The 6 samples were placed on the shaker at rpm 180. Afterwards, removing each sample at a different time, then by using the spectrophotometer, the determination of optimum contact time at which the best percent removal was achieved.

2.2 pH Optimization

The second experiment is changing the pH while the adsorbent dosage, the initial concentration of methyl red, and the contact time are fixed like the precious experiment (Taking the optimum contact time obtained from the first experiment).

2.3 Concentration Optimization

The third experiment is changing the initial concentration of methyl red with 5 samples varying from 0.1 to 0.5 mg/l. The pH and the contact time are obtained from the two previous experiment (optimum pH was equal to 4 and optimum contact time was equal to 90 mins). While the adsorbent dosage is fixed at 0.16 g.

2.4 Dose of Oxidized Chitosan Optimization

The fourth experiment is changing the adsorbent dosage by using 5 different masses of hydroxyapatite 0.02g, 0.04g, 0.08g, 0.12g, and 0.16g. While the contact time, pH, and the initial concentration are fixed at their optimum value obtained from previous three experiments.

Filter paper of 7 cm diameter were used to filter the solution after the adsorption process (after the mixing on the shaker). The Rpm of the shaker was fixed at 180 rpm throughout the four experiments. The dye used in the four experiment was methyl red, however the adsorbent used in the four experiments was the hydroxyapatite. Spectrophotometer was used after the adsorption process of each experiment to determine the optimum value of each experiment by measuring the adsorbance of the sample.

3.RESULTS AND DISCUSSION

3.1 Standard Curve

As shown in the standard curve table, that at different concentrations of Methyl red, different values of absorbance in (nm) are given by the spectrophotometer, as the concentration of methyl red increase the values of absorbance increase giving the shown values in Figure 1.

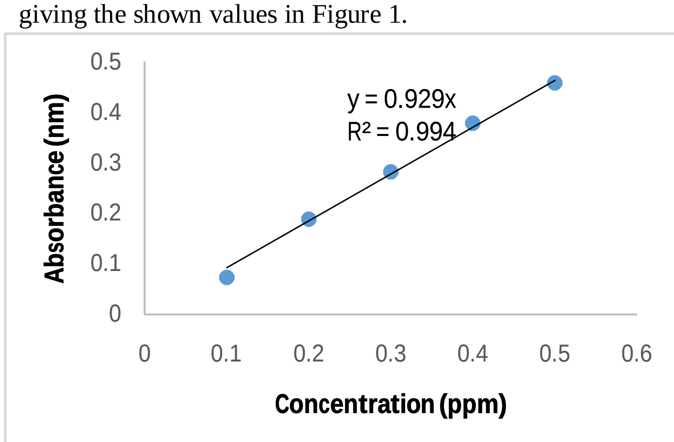

Figure 1: The relation between thymol blue concentration and absorbance

This figure shows the relation between the concentration of methyl red and the absorbance value given from the spectrophotometer, fitting the line on the best fit of dots to give a straight line, where concentration of methyl red is on x-axis and absorbance on y-axis. Also, $R^2$is calculated showing a promising result having a value of 0.9945. This relation was plotted to make it easy for each experiment to get the concentration of the dye after adsorption to know how much of it is adsorbed on the surface of hydroxyapatite, knowing the optimum condition in each experiment, where the least value of methyl red concentration after adsorption gives the optimum condition of the experiment whatever any experiment.

3.2 OptimumTime

Table 1: The relation between methyl red concentration and time of adsorption

	Time (min)	Absorbance (nm)	Concentration After Adsorption (ppm)	% Removal
	5	0.068	0.073	85.37
	10	0.038	0.041	91.82
	20	0.035	0.038	92.47
	30	0.029	0.031	93.76
	60	0.02	0.022	95.70
Optimum time	**90**	**0.012**	**0.013**	**97.42**

Adsorption experiments have been performed under the following conditions; pH = 4, initial dye concentration = 0.5 ppm and adsorbent dose = 2 g/L to determine the equilibrium time at which the dye removal efficiency reached its maximum value as represented in Table 1.

3.3 pH Parameter

Table 2: represent the effect of changing pH on the Methyl Red removal efficiency where it increased from 89.88 % to 91.6 % with increasing in pH from 2 to 4. When pH increased from 6 to 12, the removal efficiency decreased from 89.66 % to 83.85 due to increasing in the OH^- so, negative charge in solution increased and thus, the dye adsorption efficiency decreased.

Table2: The relation between thymol blue removal percentage and pH

	pH	Absorbance (nm)	Concentration After Adsorption (ppm)	% Removal
	2	0.047	0.051	89.88
Optimum pH	**4**	**0.039**	**0.042**	**91.61**
	6	0.048	0.052	89.67
	8	0.053	0.057	88.59
	10	0.071	0.076	84.72
	12	0.075	0.081	83.86

3.4 Optimum Initial Concentration

Table 3: represented the effect of changing initial dye concentration on the Methyl Red removal efficiency where it increased from 94.62 % to 83.21 % with increasing in initial dye concentration from 0.1 to 0.5 ppm. This might be occurred due to the enhancement of reaction probability between Methyl Red and Hydroxyapatite.

Adsorption experiments have been performed under the following conditions; optimum contact time = 90 min, optimum pH = 4 and adsorbent dose = 2 g/L in order to know the optimum dye concentration at which the dye removal efficiency reached its maximum value.

Table 3: Determination of the optimum dye concentration

	Initial Conc. (ppm)	Absorbance (nm)	Conc. After Adsorption (ppm)	% Removal
Optimum Conc.	**0.1**	**0.005**	**0.005**	**94.62**
	0.2	0.02	0.021	89.23
	0.3	0.035	0.037	87.44
	0.4	0.053	0.057	85.74
	0.5	0.078	0.083	83.21

3.3 Optimum Dose of Adsorbent

Table 4 represent the effect of changing adsorbent dose on the dye removal efficiency. As when the adsorbent dosage increased from 0.25 to 2 g/L; the dye removal percentage increased from 82.13 % to 94.61 % because, the available active sites increased with increasing in the adsorbent dose and thus, the Methyl Red dye removal efficiency increased. The maximum dye removal efficiency was achieved at adsorbent dose = 2 g/L.

Table 4: Determination of the optimum adsorbent dose

	Adsorbent dose (g/L)	Absorbance (nm)	Conc. after Adsorption (ppm)	% Removal
	0.25	0.083	0.089	82.13
	0.5	0.061	0.065	86.87
	1	0.038	0.040	91.82
	1.5	0.031	0.033	93.32
Optimum adsorbent Dose	**2**	**0.025**	**0.026**	**94.61**

3.4 Kinetic Study

3.4.1 First order Kinetics

The linear form of this equation is expressed as followed:
Equation 1 (Pseudo First order linear form)

$$\ln(qe - qt) = lnqe - k1t \qquad (1)$$

Where qe (mg/g) is the amount of adsorbed adsorbate at equilibrium, however, qt (mg/g) is the amount of adsorbed adsorbate at time *t*, and k_1 is the pseudo first order rate constant.

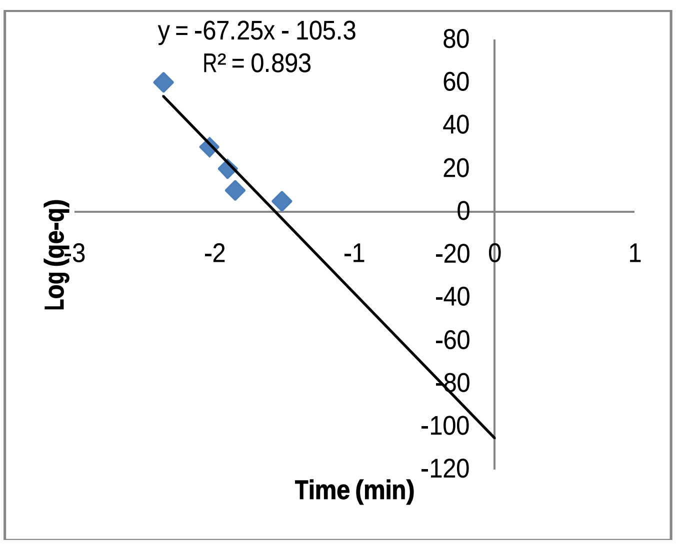

Figure 2: First order chart

Figure 2 represent the calculations performed based on using the Pseudo First Order kinetic equation. The correlation coefficient R^2 value= 0.8933, K_1 = 154.88 min^{-1}.

3.4.2 Second order kinetics

The linear expression of pseudo second order kinetics is expressed as followed
Equation 2 (Pseudo second order linear expression)

$$\frac{1}{qt} = \frac{1}{k2qe^2} + \frac{1}{qe}t \qquad (2)$$

Where K_2 is describes as the rate constant of pseudo second order equation in (g/mg min).
Figure 4 represent the calculations performed based on using the Pseudo Second Order kinetic equation and the correlation coefficient R^2 value which equalled to 0.9997, K_2 = 6.249 mg/g.min.

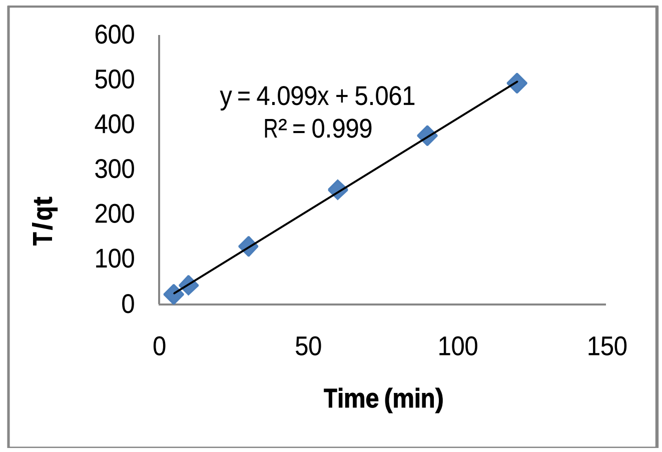

Figure 3: Second order chart

According to the R2 values of the mentioned kinetics models; it could be deduced that the best fitted kinetic model to the experimental data is the Second Order kinetic model as it had the higher R2 value than the First Order model. In addition, this deduction indicated that the type of this adsorption is a chemisorption adsorption system. Therefore, it is necessary to determine the rate controlling step of this reaction and this could be achieved using Intra-Particle Diffusion model and Boyd plot.

3.4.3 Intra-particle Diffusion Model

The intraparticle diffusion equation is expressed as:
Equation 0 (Intraparticle diffusion expression)

$$qt = kit^2 + c \qquad (3)$$

Where qt is the amount of the adsorbate at time *t*, and ki is the rate constant of the intra-particle diffusion model.
Figure 4illustrate the intra-particle diffusion model plot where the first linear portion represented the occurrence of film diffusion followed by another linear portion which represented the occurrence of intra-particle diffusion. Figure 36 represented Boyd plot where the straight line did not pass the origin which indicated that the actual rate limiting step is the film diffusion.

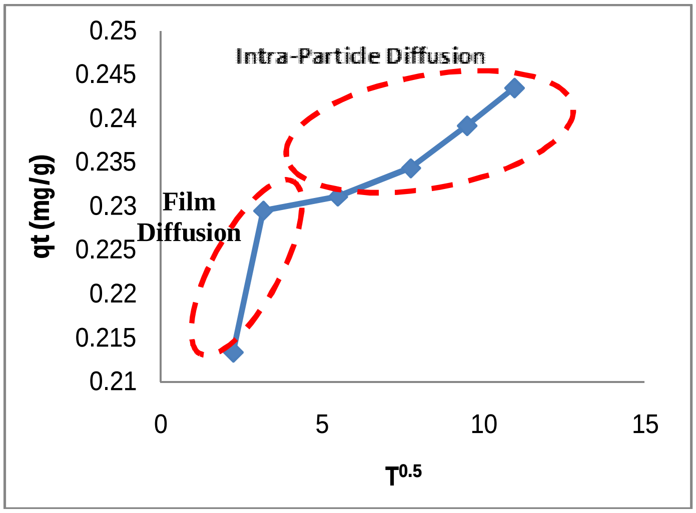

Figure 4: Intra-particular diffusion chart

3.5 Adsorption Isotherm models

3.5.1Langmuir Isotherm

This model was used at first to explain the adsorption process of mixture phases, it is also used to quantify the adsorbent capacity. Langmuir isotherm balance the rate of adsorption and desorption which is called a dynamic equilibrium.

Equation 4 (Langmuir isotherm equation)

$$\frac{1}{qe} = \frac{1}{qmKlCe} + \frac{1}{qm} \quad (4)$$

Where (qe) is the amount of adsorbed adsorbate per unit weight of adsorbent, (Ce) is the amount of un adsorbed adsorbate concentration in the solution at equilibrium. (Kl) is the Langmuir equilibrium constant, and (qm) is the theoretical monolayer saturation capacity.

Equilibrium isotherm study was performed at different dye concentrations ranged from 0.1 to 0.5 ppm and under the following conditions; pH = 4, adsorbent dose = 2 g/L and contact time = 90 min. and Figure 5 represent the Langmuir isotherm calculations, the calculated constants and R^2 value of Langmuir isotherm model; R^2 = 0.9251, q_{max} = 0.2936 mg/g and K_L = 25.11 L/mg.

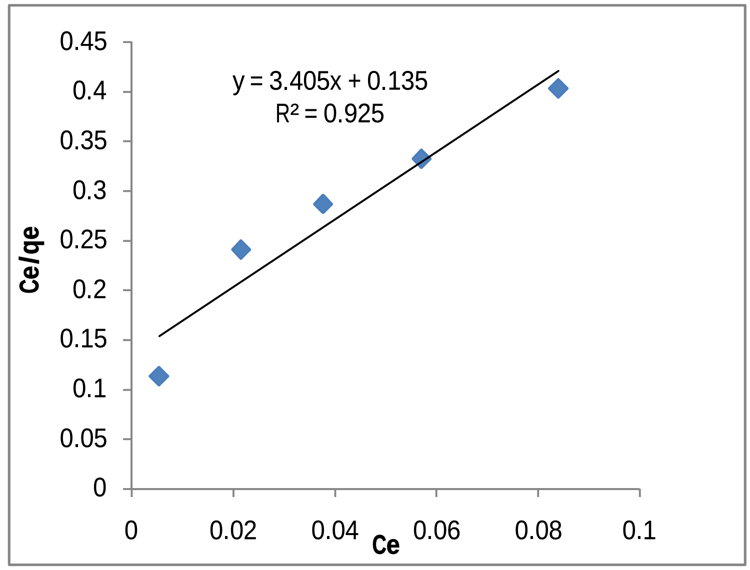

Figure 5: Langmuir isotherm chart

3.5.2Freundlich Isotherm

Equation 5 (Freundlich isotherm equation)

$$\log(qe) = \log kf + \frac{1}{n}\log Ce \qquad (5)$$

When Kf is the Freundlich constant and n is the Freundlich exponent.

Figure 6represented the Freundlich isotherm calculations, the calculated constants and R^2 value of the model where; R^2 = 0.9926, K_F = 0.793 L/mg and n = 1.82.

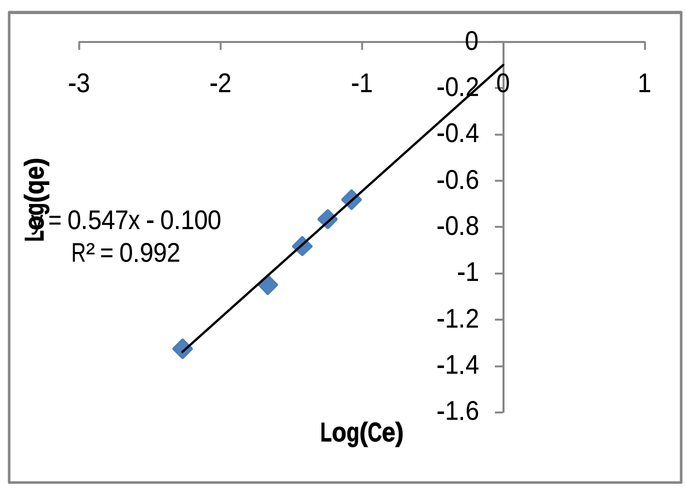

Figure 6: Freundlich isotherm chart

The R^2 value shows the suitability of the adsorption process for the Freundlich isotherm model. This result indicates the surface of the adsorbent is heterogeneous and the adsorption process functioned under multilayer adsorption.

3.5.3Halsey Isotherm

This model is usually used to evaluate multilayer adsorption process, away from the surface.

Equation 6(Halsey isotherm equation)

$$lnqe = \frac{1}{nh} lnCe + \frac{Kh}{nh} \quad (6)$$

Where $n_H$and K_H are the Halsey isotherm constants and by plotting lnqe with lnCe.

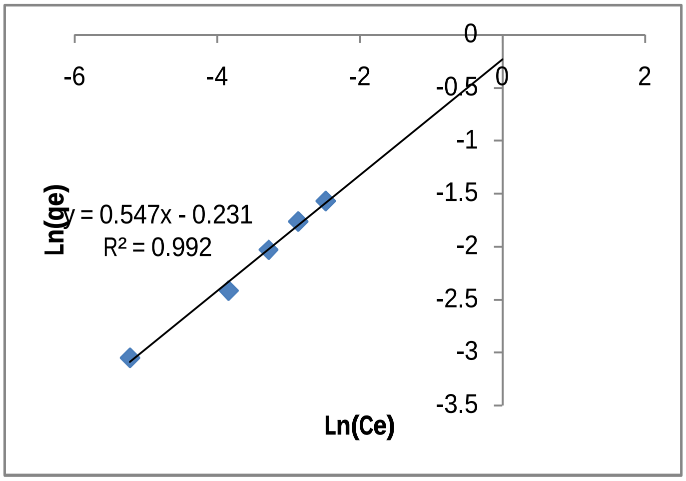

Figure 7: Halsey isotherm chart

Figure 7represent the Halsey isotherm calculations, the calculated constants and the R^2 value of the model where; R^2 = 0.9926, n_H = 1.82 L/mg and K_H = 0.423. The R^2 value of this model indicated that the adsorption of Methyl Red using Hydroxyapatite was suitable for Halsey isotherm model also, these results actually gave another proof beside the Freundlich isotherm model that the adsorption process type is chemisorption – multilayer adsorption process.

3.5.4 Dubinin-Radushkevich Isotherm

Dubinin-Radushkevich Isotherm model is used to explain the mechanism of the adsorption process with Gaussian energy distribution on heterogeneous surfaces. Furthermore, since it assumes a multilayer adsorption involving Van Der Waals forces, it is usually used to detect the difference between physical and chemical adsorption.

Equation 7 (Dubinin-Radushkevich Isotherm equation)

$$ln(qe) = BR^{\wedge}2T^{\wedge}2\, Ln^2\,(1+(1/Ce)) \; + ln\,(qmax)(7)$$

Qs is the theoretical isotherm saturation capacity, K is the Dubinin-Radushkevich constant.

Equation 8 (Ɛ equation)

$$Ɛ = RTln(1 + \frac{1}{Ce}) \qquad (8)$$

Where R is the gas constant, T is the absolute temperature (K), and Ce is the adsorbate equilibrium concentration.

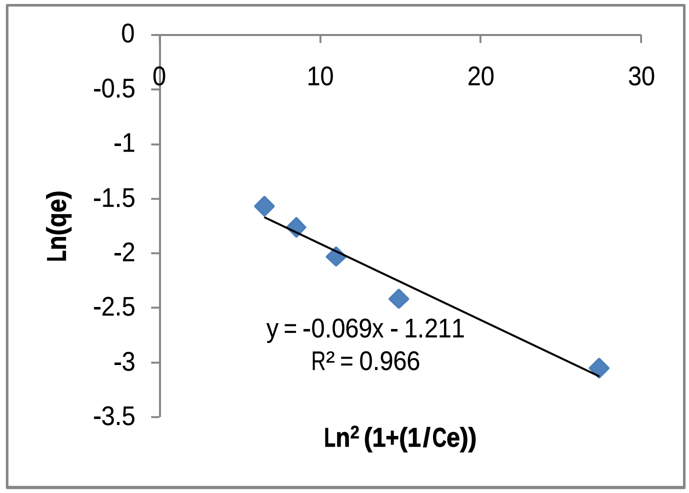

Figure 8: Dubinin-Radushkevich isotherm chart

Figure 8 represented the Dubinin-Radushkevich isotherm calculations, the calculated constants and the R^2 value of this model where; R^2 = 0.9665, q_{max} = 0.297 mg/g, and E = 6629.65 kJ/mol. If the value of E is lower than 8 kJ/mol. Therefore, the adsorption type will be physical adsorption but, here the value of E is higher than 8 kJ/mol which indicated that this adsorption process was a chemisorption process.

According to the R^2 value of previous two-parameter isotherm models; the best fitted models with the experimental data are the Freundlich and Halsey isotherms because, they had the higher R2 values than the other models.

4. CONCLUSION

Dyes and colours discharged directly in water bodies from leather and textile industry, becomes a major environmental problem because some of these dyes are toxic and non-biodegradable. The removal of these dyes becomes essential. The treatment of these dyes by the adsorption technique is the most efficient and economical. In this paper, the methyl red is being removed by using the Hydroxyapatite as an adsorbent. The experiment was carried away by changing four parameter each time. The changing parameters were time, pH, initial concentration, and adsorbent dosage. The optimum time was found to be 90 minutes with a 97% removal, the optimum pH was found to be 4 with a 91% removal, the optimum initial concentration was found to be 0.1 ppm with a 94% removal and finally the optimum adsorbent dosage was found to be 2 g/l with 94.6% removal. The equilibrium data were tested with

adsorption isotherms models. The adsorption best fitted Freundlich, and Halsey isotherms which means that the adsorbent had a heterogeneous surface according to the two parameter isotherms. Pseudo first order and pseudo second order were made to test the kinetic data, and it was found that the adsorption is pseudo second order kinetics. The mechanism of the adsorption was analysed by using the intraparticle diffusion model. The intraparticle diffusion depended on the ionic state of the dye. For future recommendation, decreasing the particle size of the adsorbent and increasing the temperature enhance the adsorption process. Moreover, using nano technology will develop the adsorption process by increasing the surface area of the adsorbent which will increase the efficiency of the adsorption process.
Finally, from this study, it can be concluded that, the Hydroxyapatite is an effective and eco-friendly adsorbent for the removal of dyes.

REFERENCES

1. AbideenIdowu Adeogun, E. A. (2018). Biowaste-Derived Hydroxyapatite for Effective Removal of Reactive Yellow 4 Dye: Equilibrium, Kinetic, and Thermodynamic Studies. India: ACS Omega.
2. Agency, U. S. (2020). Ion Exchange. Retrieved from EPA: https://iaspub.epa.gov/tdb/pages/treatment/treatmentOverview.do?treatmentProcessId=263654386
3. Shehta H. M. (2020). Development of Novel Adsorbent for Industrial Waste Water Treatment. IJATCSE, 9, 704-712.
4. Ahmed Ragab, I. A. (2019). The Removal of Brilliant Green Dye from Aqueous Solution Using Nano Hydroxyapatite/Chitosan Composite as a Sorbent. Saudi Arabia: Molecules.
5. Alqaragully, M. B. (2014). Removal of textile dyes. International Journal of Advanced Research in Chemical Science (IJARCS), 48-59.
6. Dabrowski, A. (2001). Adsorption-from theory to practice. Poland: Elsevier science.
7. Dr.V.Krishnasamy. (2016). Biosorption of Thymol Blue. India: Bharath University.
8. Fleming, G. (2014). The Activated Sludge Process. Pennsylvania: Pennsylvania Department of Environmental Protection.
9. Gabelman, A. (2017, July). Adsorption Basics. Retrieved from AlchE: https://www.aiche.org/publications/cep
10. Grosicki. (1988). Watson's Textile Design &Colour. Woodhead Publishing: Bombay.
11. Hunger, K. (2003). Industrial Dyes. Frankfurt: Die Deutsche Bibliothek.
12. Kakhia, T. (2014). DYES, COLORS & PIGMENTS. Syria: The Higher Council of Arab Union Chemists.
13. L.L. Hench, J. A. (1998). Dry production of hydroxyapetite. CeramSoc, 1705.
14. M. El-Kholy, A. K. (1998). Hydroxyapetite production. Interceram, 29.
15. M.A. Nazeer, E. Y. (2017). Sol-Gel. OpenSci, 171.
16. Morsy, R. (2015). Synthesis and physicochemical evaluation of hydroxyapatite gel biosorbent for toxic Pb(II) removal from wastewater. Arab J SciEng : King Fahd University of Petroleum & Minerals .
17. Mousavi S.A, M. M. (2017). Methylene Blue. Global NEST, 697-705.
18. Prado, P. A. (2019). A brief review on hydroxyapatite production and use in biomedicine. Scielo, 36.
19. WHO. (1999). Water treatment.