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USE OF A SPECIFIC TYPE OF BENTONITE CLAY FOR REMOVAL OF HALOGENATED ORGANIC COMPOUNDS FROM POLLUTED WATER UNDER DIFFERENT OPERATION CONDITIONS

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Abstract: Recently, the products of dyes and phenols that effluent into water cause serious environmental complications where they cannot be controlled and sustained in the environment. In this study, a special type of bentonite clay was used to remove two types of reactive dyes (red, green) and 2,4-dichlorophenol from water by adsorption processes, under different operating conditions of pH values between (4-9) contact time (30-180) min, bentonite dose (0.2-1) g/200 ml, initial concentration (5-100) mg/L for reactive dyes, and (5-50) mg/L for 2.4-Dichlorophenol.The adsorption model has been applied to represent fit the experimental data of the adsorption process. The results showed that the Langmuir model was more suitable to represent the removal of reactive dyes (red, green) and the Freundlich model was more suitable to represent the removal of 2,4-dichlorophenol by bentonite clay.

Keywords: *Reactive dye, 2,4-dichlorophenol, bentonite clay.*

أستخدام نوع خاص من طين البنتونايت لازالة المركبات الهالوجينية العضوية من الماء الملوث تحت الظروف التشغيلية المختلفة

الخلاصة: في الآونة الأخيرة ، ان منتجات الأصباغ والفينولات التي تطرح إلى الماء تسبب مضاعفات بيئية خطيرة حيث لا يمكن السيطرة عليها واستدامتها في البيئة. في هذه الدراسة ، تم استخدام نوع خاص من طين البنتونايت لإزالة نوعين من الأصباغ التفاعلية (ألحمراء، ألخضراء) و 2،4-ثنائي كلورو فينول من الماء بواسطة عمليات الامتزاز ، تحت ظروف تشغيل مختلفة لقيم الأس الهيدروجيني بين (4-9) وقت الاتصال (30-180) دقيقة ، جرعة البنتونايت (0.2-1) غرام/200 مل ، التركيز الأولي (5-100) ملغرام/لتر للاصباغ التفاعلية و(5-50) ملغرام/لتر 2،4-ثنائي كلورو فينول. تم تطبيق نموذج الامتزاز لتمثيل نتائج البيانات التجريبية المناسبة لعملية الامتزاز. أظهرت النتائج أن نموذج لانكموير كان أكثر ملائمة لتمثيل إزالة الأصباغ التفاعلية (الحمراء والخضراء) وكان نموذج فريندلش أكثر ملائمة لتمثيل إزالة 2،4-ثنائي كلورو فينول بواسطة طين البنتونايت

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1. Introduction

In the last decade, increasing number of different toxic organic and inorganic compounds has been recognized at basic levels in wastewater, surface and ground water. Human activities are causing water contamination on this planet. This water contamination is the consequences of utilizing pesticides, fertilizers, herbicides, hazardous industrial chemicals, soaps, detergents, pathogens, organic solvents, heavy metals, textile dyes and phenol product that reach their way into the water supply.

Dye wastewater generally consists of a number of contaminants, including acids, dissolved solids, toxic compounds, bases, and color. Color is the most noticeable contaminant even at very low concentrations, and it needs to be taken away or decolorized before the wastewater can be ejected [1].Textile industries produce large amounts of liquid wastes; these textile effluents contain organic and inorganic compounds. During the dyeing processes, not all dyes that are applied to the fabrics are fixed on them and there is always a portion of these dyes that remains unfixed to the fabrics and gets washed out. These unfixed dyes are found to be in high concentrations in textile effluents [2]. The reactive dyes are most used in the textile industry due to their simple dyeing procedures and their high level of stability during washing, these being the main type of dyes used to dye cellulose and cotton. Reactive dyes appeared an increasing market share, currently about 20–30% of the total market for dyes because they are used to dye cotton which makes up about half of the world's fiber consuming. A large fraction, typically around 30%, of the applied reactive dye, is wasted because of dye hydrolysis in the alkaline dye bathtub [3,4]. However, these dyes have a high solubility in the water and have a low level of fixing to fibers; most of their initial concentrations are disposed to the effluent. It’s usually characterized by aromatic dyes groups that are a serious environmental concern because of their mutagenic, carcinogenic, and inert properties [5]. The dyes have a complex aromatic structures result in thermal, physicochemical and optical stability and resistance to common wastewater treatment. When the water bodies receive the dyes that have been discharged, they produce toxic amines through reductive cleavage of azo linkages, which causes several effects on human beings by damaging the vital organs such as the liver, brain, the nervous system, kidney and reproductive systems. Moreover, the containment of synthetic dyes on aromatics, chlorides, metals, etc. This causes adversely impact on photosynthetic activity of some aquatic life. Hence their removal from aquatic environment is great importance and subject of many scientific researches [6].

The other studied pollutant in this research 2,4-dichlorophenol is organic halogen hydrocarbon consist of phenol and chlorine functional group. It’s a chemical intermediate used principally in the manufacture of the herbicide (2,4-dichlorophenoxyacetic acid), Fungicides wood preservative and pharmaceutical manufacturing. It’s also observed in the effluent of disinfected water after chlorination, in core and paper wastewater and in the flue gas of municipal waste incineration. It is considered to be hazardous substances and primacy toxic pollutants by the U.S. Environmental Protection Agency. This chemical can be toxic to human. It can damage kidneys, liver, the nervous system, blood-forming organs and it is also suspected to be human carcinogen [7]. The WHO put the permissible phenolic concentration of 0.001 mg in potable water [8]. Thus many treatment processes have been applied for the removal of them from wastewater because of toxicity of chlorinated phenolic compounds [9]. This wastewater must be treated with suitable methods before discharging to the water bodies or environment, to keep environment from different harmful effects of these compounds.

Various techniques have been developed for the removal of toxic contaminants, including adsorption, ion exchange, chemical precipitation, membrane based filtration, photo degradation, evaporation, solvent extraction and reverse osmosis [10]. Among them, Mechanism of adsorption can be found to be an excellent way to treat industrial waste effluents, show significant advantages like low-cost, availability, profitability, easy operation and efficiency and there is a variety in the use of adsorbents. Adsorption is one of the most favorable decolonization techniques in dyeing and 2,4-dichlorophenol wastewater treatment [11].

2. Materials and Methods:

2.1. Material

2.1.1 Adsorbent:

The adsorbent used in this research is natural bentonite clay .The physicochemical properties are shown in Tables 1 and 2.

Table 1. Chemical analysis of bentonite clay by XRF

Composition	Content %	Composition	Content %
SiO_2	50.459	MnO	0.021
Al_2O_3	33.235	SrO	0.018
CaO	8.043	ZnO	0.010
Fe_2O_3	5.581	ZrO_2	0.008
K_2O	1.535	CuO	0.005
TiO_2	0.501	NiO	0.003
SO_3	0.497	MoO_3	0.003
V_2O_5	0.040	Y_2O_3	0.001
Cr_2O_3	0.030	CO_2	0.010

Table 2. Properties of bentonite clay

Characteristics	value
BET surface area	57.7362 m^2/g
Pore size	7.1769 Å
Bulk density	1.2121
Real density	2.4092
Porosity %	0.49688

2.1.2 Adsorbates:

Two reactive dyes (RR, RG) and 2,4-dichlorophenol**.** Characteristic are shows in Tables 3 and 4 below:

Table 3. Table (2-A) Chemical and Physical characteristic of reactive dyes used in the study

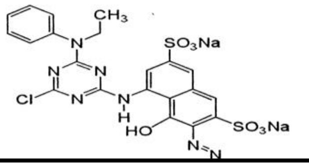
items	Reactive red	Reactive green
Trade name	Drimarene Brilliant Red P-B	Drimarene Brilliant Green Z-3G
Origin	SWITZERLAND	SWITZERLAND
Phase	Solid/Powder	Solid/Powder
Molecular formula	$C_{27}H_{19}CLN_7Na_3O_{10}S_3$	$C_{60}H_{29}CL_3N_{16}NiO_{21}S_7.6Na$
Wave length	533	660
Molecular weight	802.1	1839.4499
pH	6.5	6.5
Solubility g/L at 25°C	95	99
Chemical structure		Not disclosed by the manufacturer

Table 4. Chemical and Physical properties of 2,4-dichlorophenol utilized in the study

Items	Properties
Chemical formula	$C_6H_4Cl_2O$
Specific Gravity	(60°C/4°C)
Vapor Pressure @ 20°C	10 mm Hg
Boiling Point	419°F/215°C
Molecular Weight	163
Vapor Density (Air = 1)	5.6
Water Solubility	0.45 g/100 g
Appearance	White/off-white crystalline solid
Flash Point (TCC)	219°F/104°C

3. Adsorption experiments

3.1 Stock Solutions

Simulated stock solutions of 1000 mg/L were prepared by dissolving one grams of both reactive dye (RR, RG) and 2,4-Dichlorophenol in one liter of distilled water then diluted to the desired solution concentration of the single dyes (RR, RG) and 2,4-Dichlorophenol. All experiments were conducted in sanitary laboratory of environmental engineering department at temperature (25±2)°C.

3.2 Calibration Curves

The calibration curves of two dyes (RR, RG) and 2,4-Dichlorophenol were prepared to find unknown concentrate value after treatment, in which standard solutions have different concentrations from (5-100) ppm for two dyes and (5-50) ppm for 2,4-Dichlorophenol was prepared using distilled water as a solvent and the absorbance for each sample solution was measured using a spectrophotometer thermo-Genesis 10 UV technique visible.

3.3 Batch Adsorption Study

In this experiment, a batch adsorption technique was used. To study the effects of various important parameters such as amount of adsorbent, pH values, the contact time between adsorbate and adsorbent. Weights of 0.2, 0.4, 0.6, 0.8 and 1g of bentonite clay were added each time to conical flasks containing 200 mg/L solution of RR, RG and 2,4-Dichlorophenol separately. The mixture was placed in a shaker orbital (Gemmy orbit shaker, Model: VRN-480, USA,) at 200 rpm Speed of mixing, while pH of the solution varied between 4, 7 and 9 by adding 0.1N HCL or 0.1N NaOH to get the desired pH by using pH-meter. Samples were withdrawn from the stirrer at different time intervals. Then the adsorbents were separated from the sample by using filter paper. The absorbance was measured for supernatant solution using UV-Spectrophotometer. Finally results were plotted where the equilibrium concentration of dyes and 2.4-dichlorophenol removed (%). Extensive sets of experiments were conducted at different time intervals (30, 60, 90, 120 and 180 minutes). The amount of adsorption at equilibrium time, q_e (mg/g) was calculated using eq. (1):

$$q_e = (C_0 - C_e)\,\mathrm{V}/W \qquad (1)$$

Where;

C_0 is the liquid-phase concentrations of adsorbent at initial (mg/L).

C_e is the liquid-phase concentrations of adsorbent at equilibrium (mg/L).

V is the volume of the solution, L.

W mass of dry adsorbent used, g.

4. Result and Discussion

4.1 Initial concentration Effect

Study the initial dye and 2,4-Dichlorophenol concentration effect by varying from 5 to 100 mg/L. The maximum removal is 43.612, 86.5 and 61% for RR, RG and 2,4-Dichlorophenol, respectively which was found at initial concentration of 25 mg/L for RR ,RG and 15 mg/L for 2,4-Dichlorophenol. According to The results shown in Fig. 1, 2 and 3, the explanation for this behavior is in case of the higher initial concentrations, the greater the number of molecules competing on the sites available on the surface of the bentonite clay. If the concentrations were low for (RR, RG) dyes and 2,4-dichlorophenol, the adsorption sites available were higher and the higher adsorption yields were obtained. The adsorption removal ratio was found to increasing somewhat and then decrease with the increase of the initial concentrations for (RR, RG) dyes and 2,4-Dichlorophenol due to the saturation of both surface area and active sites of adsorbents and is consistent with the study [12].

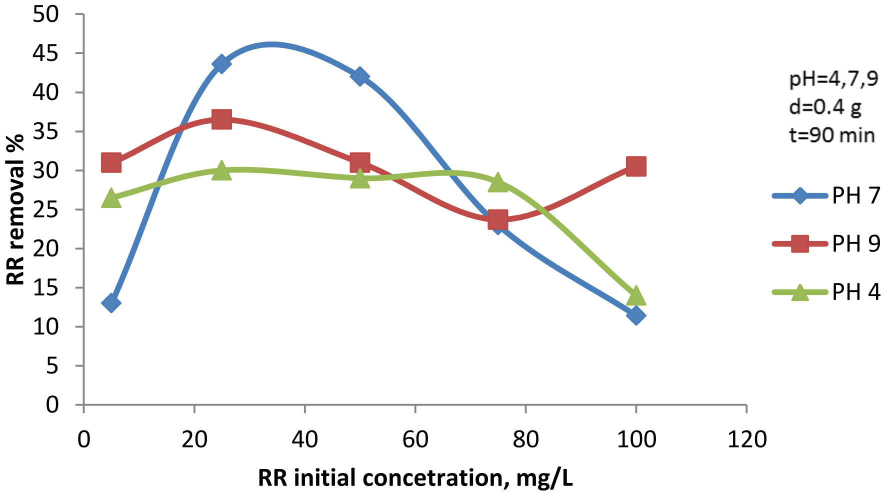


Figure 1. Effect of initial concentration on the removal efficiency of RR.

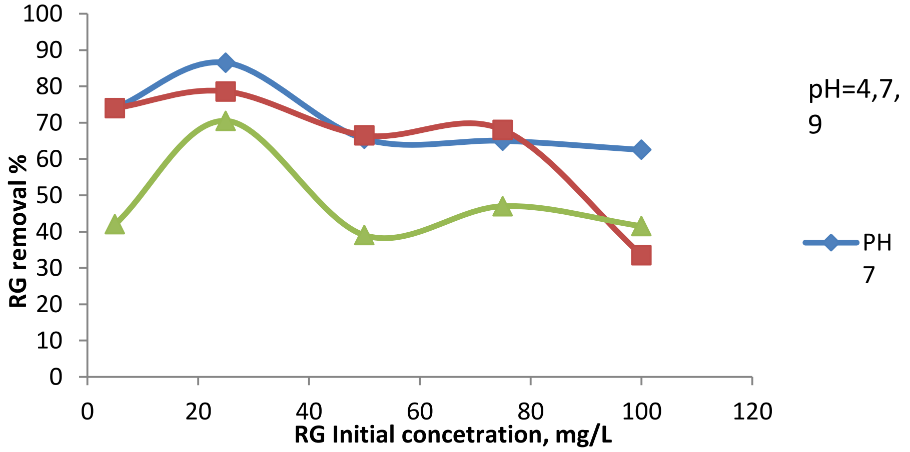


Figure 2. Effect of initial concentrations on the removal efficiency of RG.

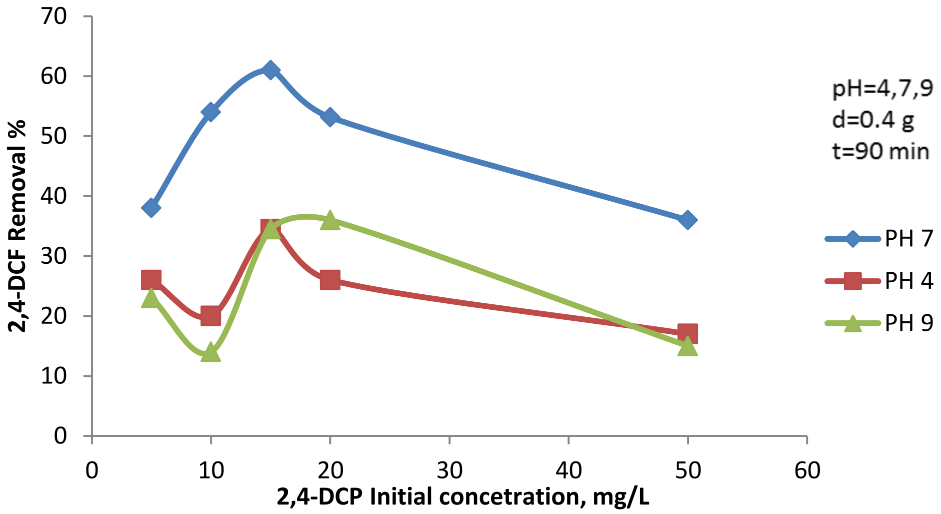


Figure 3. Effect of initial concentration on the removal efficiency of 2, 4-DCP.

4.2 Effect of pH

In this study the pH value was changed from (4-7 and 9) to cover pH range (acidic, neutral and basic) The adsorption removal efficiency of dyes and 2,4-Dichlorophenol was increasing in neutral at pH =7. The pH effects on the removal efficiency of reactive dyes and 2,4-Dichlorophenol is shown in Fig. 4, where at low pH, the surface charge may be positive , Making ions (H+) competing effectively with adsorbates causing a decrease due to the electrostatic repulsive force between positively charged adsorbates and positively charged adsorbed surface. In the case of an increase in pH, the increase of OH− ions, which leads to competition with dyes and 2,4-Dichlorophenol anions of bio sorption sites, resulting in a decrease in the removal of adsorbents in the case of bentonite clay, which is positively-negatively charged adsorbent. These results are consistent with [13].

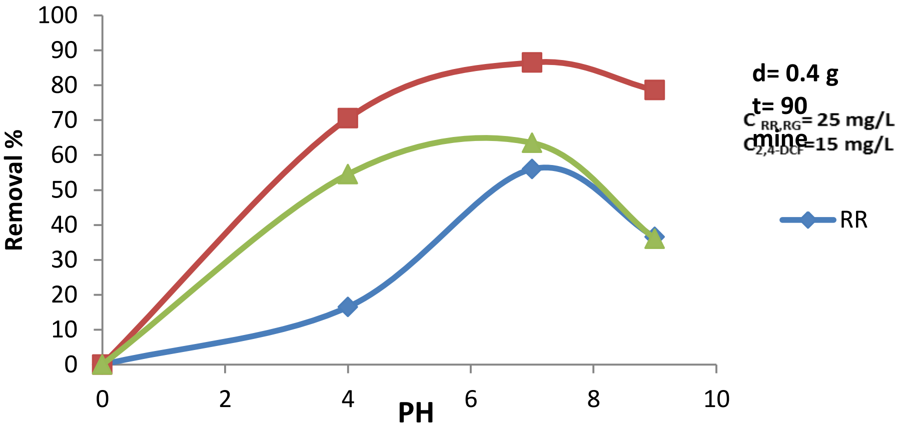


Figure 4. pH Effect on the Removal efficiency of RR, RG and 2,4-Dichlorophenol.

4.3 Contact time effect

The optimum contact time was found at 120 min for both reactive dyes and 2,4-Dichlorophenol with maximum removal efficiency of 57.59, 90.11 and 63% for RR, RG and 2,4-Dichlorophenol, respectively and Noting that the green dye gives removal efficiency after 40 minutes about 85% so it is more economical in terms of time.

As shown in Fig. 5 the adsorption percentage increases by increasing the contact time; however, adsorption ratio reached to equilibrium after 120 min. With regarding to present study, the reactive dye (Red, Green) and 2,4-Dichlorophenol removal efficiency increased by increasing contact time which was due to more contact between pollutants and adsorbent.

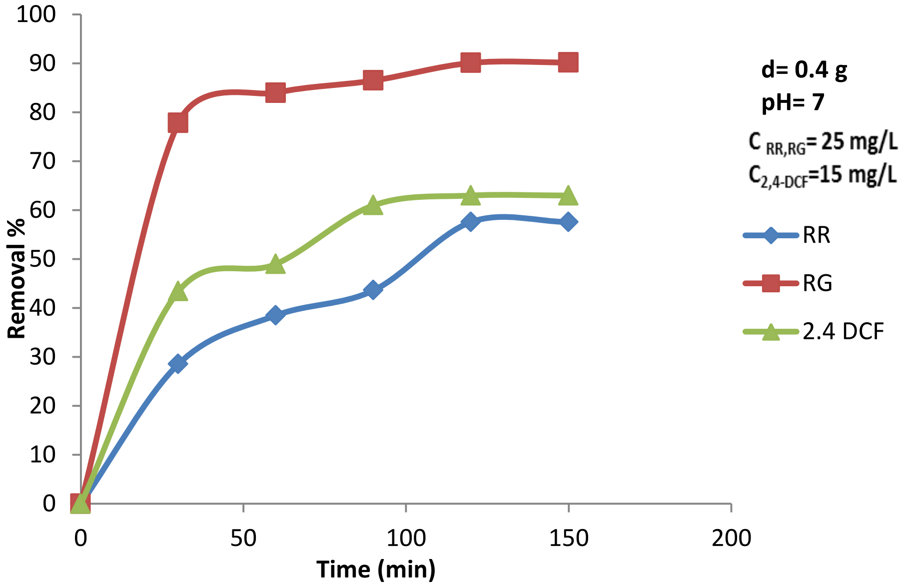


Figure 5. Contact time effect on the removal efficiency of RR, RG and 2,4-DCP.

4.4 Effect of bentonite dosage

The optimum amount of bentonite dosage was found to be 1g for RR and 0.8g for RG and 2,4-Dichlorophenol which was used for all subsequent adsorption studies. The removal efficiency at these doses was 65.6, 95.26 and 69% for RR, RG and 2,4-Dichlorophenol, respectively.

As shown in Fig. 6, the increase in adsorption capacity with the increase in the adsorption dose occurs as a result of the increase in the surface area, which leads to an increase in the total number of empty sites due to the increase of mass adsorbents. This corresponds to previous studies [14].

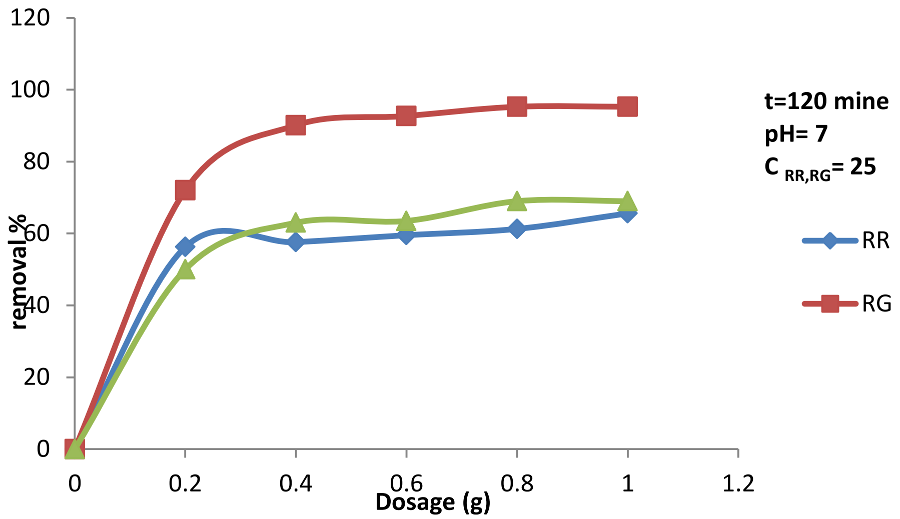


Figure 6. Effect of adsorbent dosage on the removal efficiency of RR, RG and 2,4-Dichlorophenol.

5. Adsorption Isotherm:

In order to describe the equilibrium properties of adsorption in the current study two isothermal equations, namely Langmuir and Freundlich were used. The Langmuir and Freundlich isotherm is most frequently used to represent the data of adsorption from solution. The isotherm studied was carried out for optimum condition. The adsorption data were analyzed according to the linear form of the Langmuir isotherm equation. In order to establish the maximum adsorption capacity, the Langmuir isotherm equation of the following linearized form was applied to the sorption equilibrium at different adsorbents doses. The isotherm is described by the following eq. 2:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{k_l q_m}\left(\frac{1}{c_e}\right) \qquad (2)$$

Where:

C_e is the equilibrium dye concentration in solution (mg/L),

q_e is the adsorption capacities (amount of adsorbed per weight of adsorbent, mg/g) in equilibrium.

q_m is the adsorption capacities (amount of adsorbed per weight of adsorbent, mg/g) in any time and

K_l is Langmuir constants that can be determined from above Langmuir linear equation.

A graph of 1/q evs $1/C_e$ was plotted. The constant q_m and K_L can be evaluated from the intercept and slope of this linear plot. Fig. (7) shows the Langmuir isotherm plot $1/q_e$ versus $1/C_e$. The slope of this plot is equivalent to ($1/q_m K_L$) when it intercepts $1/q_m$.

Of The Freundlich isotherm is described by following Fig. (3):

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

Where:

K_F and n are constants of the Freundlich isotherm that signify adsorption capability and strength, respectively.

K_F and 1/*n* obtained from the intercept and slope of the linear plot of log q_e versus log C_e.

The adsorption isotherms for two reactive dyes and 2, 4-Dichlorophenol using adsorbents bentonite clay are shown in Fig. 7 to Fig. 12. Factors for both models were calculated from the experimental data, and then presented in Table 3. For both reactive dyes (red and green), the determination coefficient (R^2) for Langmuir isotherm was higher than the Fruendlich isotherm, whereas for 2,4-dichlorophenol was have highest (R^2) value. The Langmuir equation represents a very good adsorption process for the reactive red and green dyes, it means that the adsorption take places as homogeneous sites, all sites are equivalent and there are no interactions between adsorbate molecule and adjacent sites. The Fruendlich equation is a good absorption of 2,4-dichlorophenol. It indicates that a heterogeneous distribution of active sites is presented on clay.

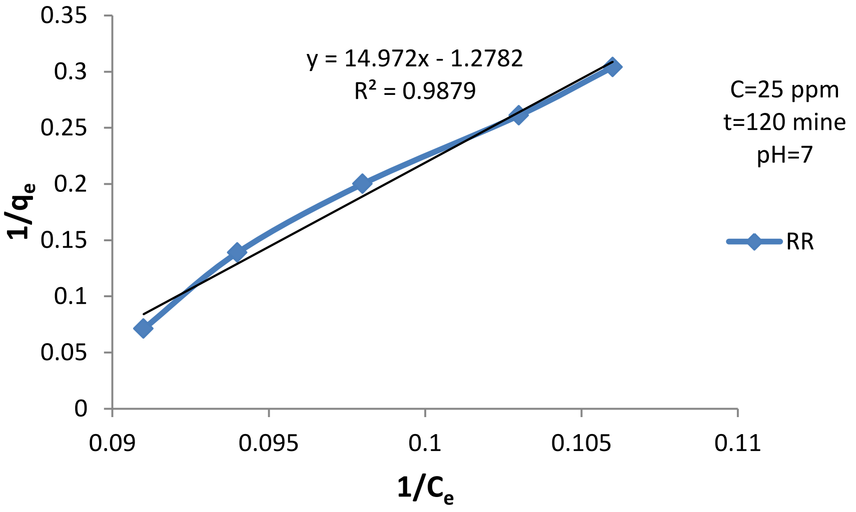


Figure 7. Langmuir isotherm for RR removal from solution using bentonite clay.

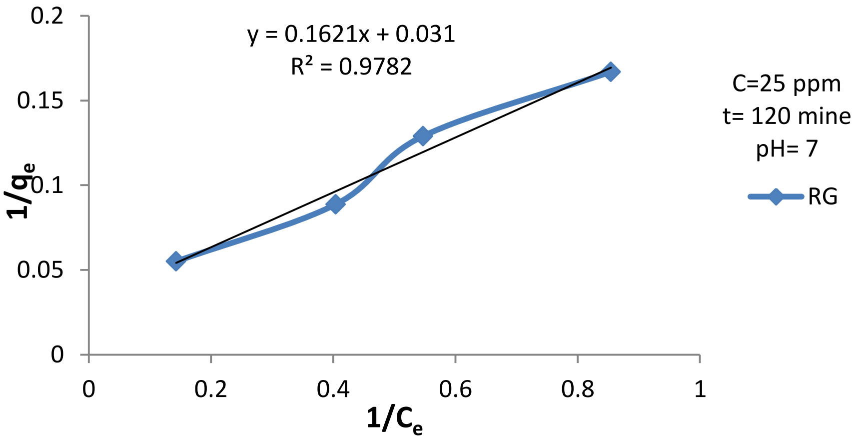


Figure 8. Langmuir isotherm for RG removal from solution using bentonite clay.

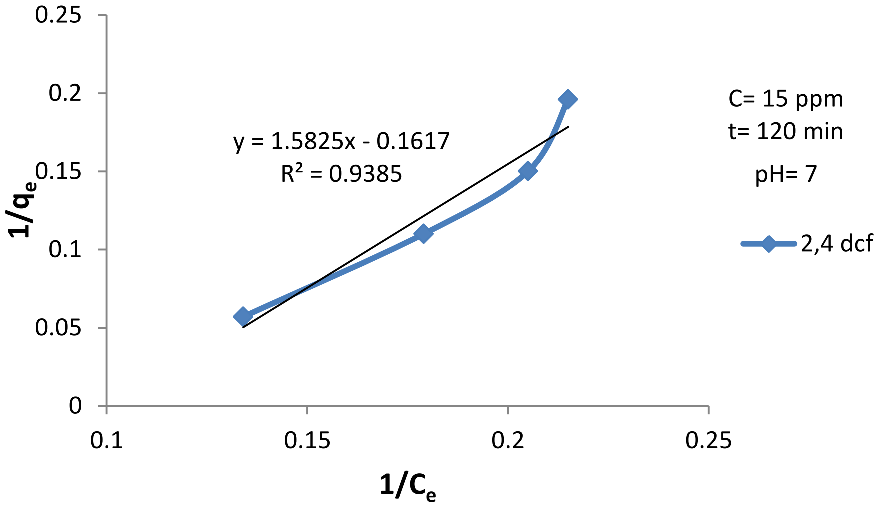


Figure 9. Langmuir isotherm for 2, 4-Dichlorophenol removal from solution using bentonite clay.

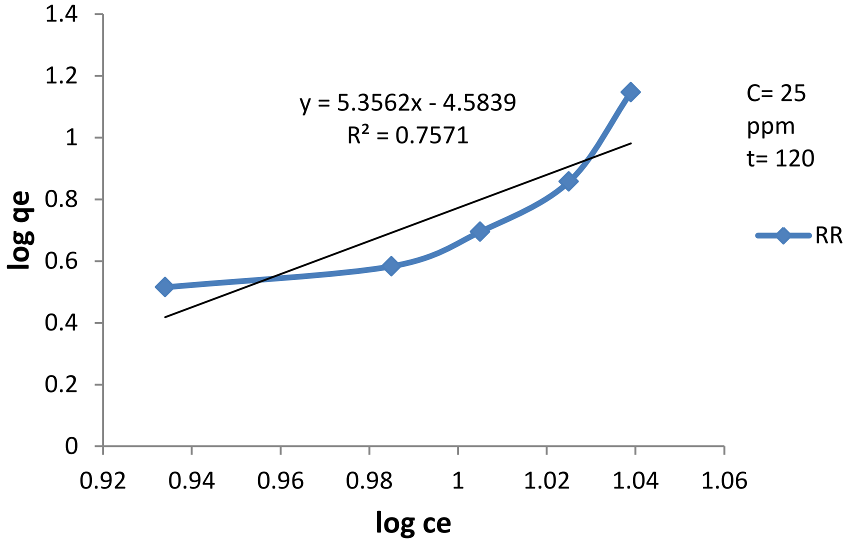


Figure 10. Freundlich isotherm for RR removal from solution using bentonite clay.

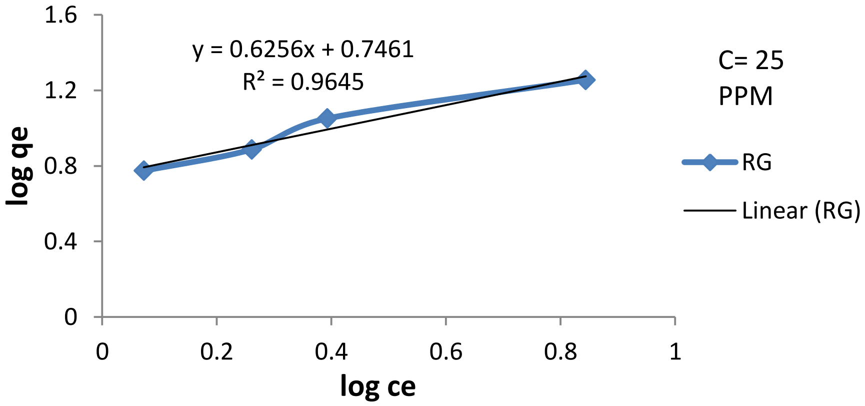


Figure 11. Freundlich isotherm for RG removal from solution using bentonite clay.

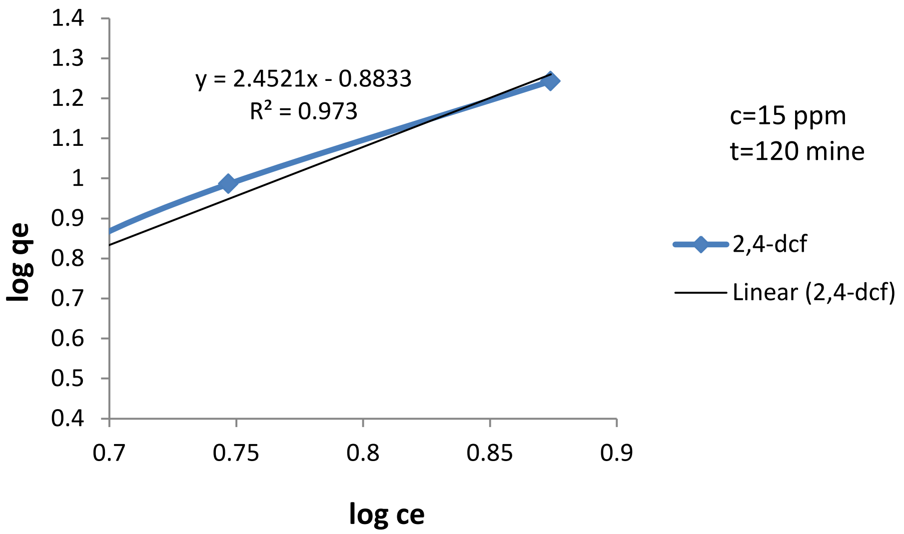


Figure 12. Freundlich isotherm for 2,4-Dichlorophenol removal from Water using bentonite clay.

Table 3. Adsorption Isotherm Models Constants

adsorbate Type	Isotherm of Langmuir $\frac{1}{q_e}=\frac{1}{q_m}+\frac{1}{k_l q_m}\left(\frac{1}{c_e}\right)$			Isotherm of Freundlich $\log q_e=\log K_F+\frac{1}{n}\log C_e$		
	K_L (mg/g)	q_m (L/mg)	R^2	K_F (L/g)	n	R^2
Reactive red	-11.73	0.0667	0.9879	2.6×10^5	-0.187	0.757
Reactive green	5.228	6.17	0.9782	5.573	1.598	0.965
2,4-DCF	-0.631	9.663	0.92	0.131	-0.407	0.973

6. Conclusions

From this study, it may be concluded that the removal of two reactive dyes and 2,4-dichlorophenol by adsorption on bentonite clay has been found to be useful for controlling water pollution, the adsorption of dyes and 2,4-dichlorophenol is influenced by pH values, amount of adsorbents and contact time. Also, the adsorption of dyes follows the Langmuir isotherm model and 2,4-dichlorophenol dyes follows the Freundlich isotherm model .optimum adsorbent dose was 1g for RR and 0.8g for RG and 2,4-dichlorophenol. The uptake of the dye increased with increasing contact time and the optimum contact time was obtained at 120 min. Also, the adsorption was found to be higher at pH 7. From this research work it can be concluded that. It is possible to design and optimize an economical treatment process for the dye and 2,4-dichlorophenol removal from industrial effluents.

7. Abbreviations

2,4-DCF	2,4-dichlorophenol
RR	Reactive red
RG	Reactive green
t	time
R^2	Correlation coefficient

8. References

1. Sukumar M1, Sivasamy A and Swaminathan G. (2017). *’’Decolonization of textile dye effluent by genetically improved bacterial strains’’.*
2. Mohamed A. Hassaan and Ahmed El Nemr. (2007). *’’Health and Environmental Impacts of Dyes’’*. American Journal of Environmental Science and Engineering. 1(3): 64-67.
3. Kunal Singha, Subhankar Maity and Mrinal Singha. (2012). *’’The Salt-Free Dyeing on Cotton: An Approach to Effluent Free Mechanism; Can Chitosan be a Potential Option’’*. International Journal of Textile Science, 1(6): 69-77
4. Arslan I. (2001). *’’Treatability of a simulated disperses dye-bath by ferrous iron coagulation, zonation, and ferrous iron-catalyzed zonation. Hazardous”* Mat.; B85: 29-41.
5. Nurhidayatullaili Muhd Julkapli, Samira Bagheri and Sharifah Bee Abd Hamid. (2014). *’’Recent Advances in Heterogeneous Photocatalytic Decolonization of Synthetic Dyes’’*. Volume, Article ID 692307, 25 pages.
6. Kamaljit Singh and Sucharita Arora. (2011). *’’Removal of Synthetic Textile Dyes From Wastewaters: A Critical Review on Present Treatment Technologies’’*. Journal Critical Reviews in Environmental Science and Technology Volume 41.
7. Li XZ, Zhao BX and Wang P. (2007). *’’Degradation of 2,4-dichlorophenol in aqueous solution by a hybrid oxidation process J Hazard Mater”.*
8. R. Subha, O.A.Sridevi, D.Anitha and D.Sudha. (2015). *’’Treatment methods for the removal of phenol from water’’*. International Conference on Systems, Science, Control, Communication, Engineering and Technology.
9. Zhao J, Lin W, Ma X, Lu Q, Ma X, Bian G and Jiang L. (2010). *’’The protein kinase Hal5p is the high-copy suppressor of lithium-sensitive mutations of genes involved in the sporulation and meiosis as well as the ergo sterol biosynthesis in Saccharomyces cerevisiae”*. Genomics; 95(5):290-8.
10. Rani Bushra, Anees Ahmed and Mohmmad Shahadat. (2017). *’’Mechanism of Adsorption on Nano materials’’.*
11. Mehali J. Mehta, Karishma K. Chorawala. (2014). *’’Adsorptive Removal Of Dye From Industrial Dye Effluents Using Low-Cost Adsorbents’’*. Mehali J. Mehta Int. Journal of Engineering Research and Applications, pp.40-44.
12. P. Sathishkumar, M. Arulkumar and T. Palvannan. (2012). *’’Utilization of agro-industrial waste Jatropha curcas pods as an activated carbon for the adsorption of reactive dye Remazol Brilliant Blue R (RBBR)”* Journal of Cleaner Production 22 (1), 67-75.
13. D. A. Fungaro, M. Yamaura, and T. E. M. (2011). *’’Carvalhos Adsorption of anionic dyes from aqueous solution on zeolite from fly ash-iron oxide magnetic*

nanocomposite''. Chemical and Environmental Technology Center, Nuclear and Energy Research Institute، P.C. 11049, São Paulo, Brazil.

14. N. Yeddou and A. Bensmaili. (2005). *''Kinetic models for the sorption of dye from aqueous solution by clay-wood saw dust mixture''*, Desalination, 185, 499-508.