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Removal of Remazol Brilliant Blue from Aqueous Solution by Iraqi Porcelanite rocks

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Abstract : It has been studied to removal Remazol Brilliant Blue dye from Aqueous Solution by Iraqi Porcelanite rocks. Conducted a series of experiments have been evaluated several experimental variables included initial dye concentration, contact time, adsorbent dose, initial pH, and temperature. Results showed a maximum absorption of Remazol Brilliant Blue dyein optimal conditions are initial dye concentration (40 mg.L^{-1}), weight of adsorbent (0.06 g), pH solution (6.7)and contact time (20 min). The removal of Remazol Brilliant Blue dye using Iraqi porcelanite rocks has been studied at different temperatures (298.15, 308.15, 318.15, and 328.15)K to determine the adsorption isotherms . The shapes of the isotherms obtained from the experimental data were found to be comparable in all cases to the (S- curve) type according to Giles classification. Langmuir and Freundlich isotherm models were used to describe the experimental isotherms and isotherms constants. Equilibrium data for Remazol Brilliant Blue fitted very well with Freundlich isotherm model. Accounts indicated thermodynamic parameters such as Gibbs free energy changes (ΔG), standard enthalpy changes (ΔH) and standard entropy changes(ΔS) . The negative values of (ΔG) inremazol Remazol Brilliant Blue dye at different temperatures indicate possible spontaneous removal (adsorption/sorption)of the mentioned adsobates on leaf powder surface .The negative value for the standard entropy changes(ΔS) show the decreased randomness at the surface /solution interface to Remazol Brilliant Blue and Iraqi Porcelanite rocks. Standard enthalpy changes (ΔH) value were found to be negative indicating an exothermic nature of the removal processes.

Keywords : Adsorption, Porcelanite rocks, Remazol Brilliant Blue, isotherms, Langmuir, Freundlich.

(I) Introduction

It exacerbated the pollution problem as one of the most important environmental problems in the beginning of the twentieth century [1].Under water with the growth of the industry to pollution as using human chemicals in most of his affairs as interference in all industries , such as pesticides ,cosmetics ,medicines ,industrial fabrics ,dyes and etc[2]. Various types of dyes are widely used in many industries such as textiles, tannery, paper, leather, paint, cosmetics and food industries [3,4].Most of dyes are harmful for human health an d aquatic life[3].And water pollution can be defined as the addition of harmful substances from the human to the aquatic environment sufficient to cause harm to human life and the living organisms[1].There are so many as pects that point to water pollution ,including the lack of dissolved oxygen ,increasing the temperature ,the presence of toxic waste ,…etc[5]. Which leads to damage to health ,life and the environment and not to use the power to domestic ,industrial and agricultural purposes [6] Generally, the disposal of dyes in precious water resources has generated various treatment technologies, which ranges from physical (sedimentation, filtration, etc.), chemical (oxidation processes including use of free radicals, precipitation and electro-coagulation), physical–chemical (adsorption, ion-exchange, stripping, chemical oxidation and membrane separation), biological (aerobic, anaerobic, combined aerobic – anaerobic), acoustical, radiation and electrical processes [6,7].despite the importance of these techniques, but it is limited in use because of the high cost [7].Adsorption technology is one of the important methods in the treatment of it with a few expensive because of the availability of many natural resources that can be used adsorbent, such as [clays ,carbon ,zeolites, blocs organic, agricultural waste, etc[8,9].So various types of agro waste materials are investigated in all over the world for removing dyes and other pollutants. The Iraqi porcelanite rocks represent one of the most and great adsorbents, because it is containing high percentage of silicon reached to 50% [10].

(II) Experiments

1.Materiales used :

Porcelanite Celikatih rocks are fine grained with fabric and cross –looks like porcelain[11] .And are found in large areas within western Iraq in regions of Trebil and Akashat, best exist in Haifa region (H3) away this region around (70 Km)West of Al retba –Anbar[11,12]. There are several known types for the porcelanite are American, Russian , German ,Turkish and Algerian ,and Iraqi porcelanite compete with other types athough contain high concentrations of carbonate. Characterized by Iraqi porcelanite also its proximity to the less than iron oxide ratios compared with Russian porcelanite[11] as shown in the table (1) follows

Table (1) chemical and physical analysis for the porcelanite samples of Traifawi Site.

No.	Chemical Composition	X-Ray Analyzer%
1	SiO_2	74.0313
2	CaO	5.6296
3	MgO	3.6556
4	Al_2O_3	3.6539
5	P_2O_5	1.1600
6	Fe_2O_3	0.9794
7	TiO_2	0.1773
8	K_2O	0.1707
9	Na_2O	0.0662
10	Cr_2O_3	0.0245
11	SO_3	0.0090
12	MnO	0.0043
13	L.O.I	11.2000
	Sum	100.7617

The adsorption capacity of porcelanite is due to the large surface area within the composition of critobalite and tridymite[12,13].

The crushed and milled samples of porcelanite was washed several times with deionised water then dried to constant weight at (110 C) by using drying oven. Each sample was sieved and the fraction of 75 µm and below was collected for adsorption experiments.

Remazol Brilliant Blue R dye (C. I. 61200) was obtained from M/s. Atul Industries, India. Purity of dye was 50%. AlCl3·6H2O and NaHCO3 were purchased from S. D. Fine Chemicals Mumbai, India, and used as such. All the chemicals received were used without further purification. The bentonite clay was collected from Barmer district of Rajasthan state of India.

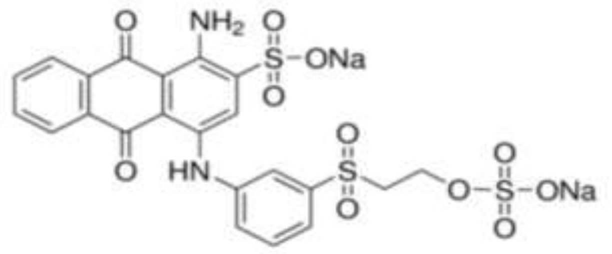


Figure 1: Structural formula of remazol Brilliant Blue dye.

2.Batch Adsorption Experiments:

The adsorption experiments were carried out by agitating(0.06g) adsorbent with (25 ml) of dye solutions 40 mg.L^{-1} at (150) rpm on an thermostated shaker water bath. unabsorbed supernatant liquid was analysed for the residual dye concentration using Shimadzu UV-Vis 1800 digital double beam at a wavelength corresponding to the λ max. The effect of pH was studied by theadjusting of pH of the adsorptive solution using(0.1 N) of HCl and(0.1 N) of NaOH solutions ,results of the experiment showed that the PH dye without adding any standard solution (6.7) and their use in experiments later. The effect of temperature was studied using four different temperatures (298 – 328 K).All experiments were carried out in duplicate and the mean values are reported .The effect of each parameter (contact time, PH value ,temperature and adsorbent dosage) were evaluated in an experiment by varying the parameter, while keeping the other parameters as constant. The amount of dye on porcelanite adsorbent was calculated using the following equation.

$Qe=(C_o - Ce)V/m$ …(1)

Where Qe (mg/g) is the amount of dye adsorbed at equilibrium (adsorbent capacity), C_o and Ce are the (mg.L^{-1})concentrations of dye at initial and equilibrium respectively, V and m is the volume of the dye solution (L) and the adsorbent mass (g) respectively.

The percentage of removable can be calculated by the following equation

$Re\% = (C_o-)/C_o * 100$ ……...(2)

(III) Results and Discussion:-

Effect of Contact Time

The relationship between contact time and adsorption capacity of Remazol Brilliant Blue dye is conducted through batch experiments to achieve the equilibrium as shown in (Figure 2). The results showed that the equilibrium time was reached within 20 mins.

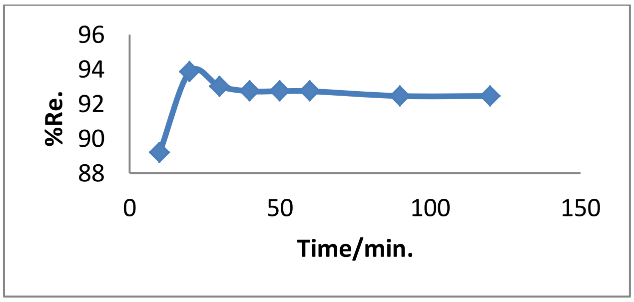


Figure 2:Effect of contact time on adsorption of: Remazol Brilliant Blue dye by Iraqi Porcelanite rocks. adsorbent Dosage = 0.06 g at 298 K.

Effect of PH

The pH is the important factor which controls the adsorption process especially for Remazol Brilliant Blue dye[15].(Figure3) shows the effect of pH for the adsorption of Remazol Brilliant Blue on to Iraqi Porcelanite rocks over a pH range of 2-12. As elucidated in (Figure 3), the dyes removal were minimum at pH 2 and the dyes adsorbed increased as the pH was increased from 2 to 6.7. Then, beyond pH 6.7 there was no notable change. For this reason, pH 6.7was selected for further experiments, and are PH dye without adding any standard solution has been relied upon experiences later. After adsorption experiments, it was found that at low pH and at high pH , the dye become protonated, the electrostatic repulsion between the protonated dye and positively charged adsorbent sites result in decreased adsorption. Higher adsorption at pH 6.7may be due to increased protonation by the neutralization of the negative charges at the surface of the adsorbent , which facilitates the diffusion process and provides more active sites for the adsorbent[15,16].

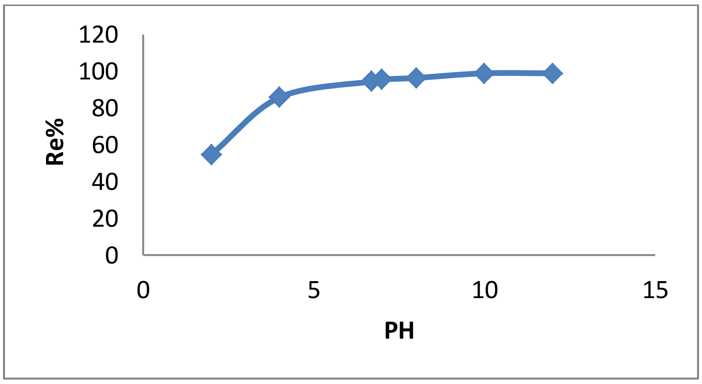
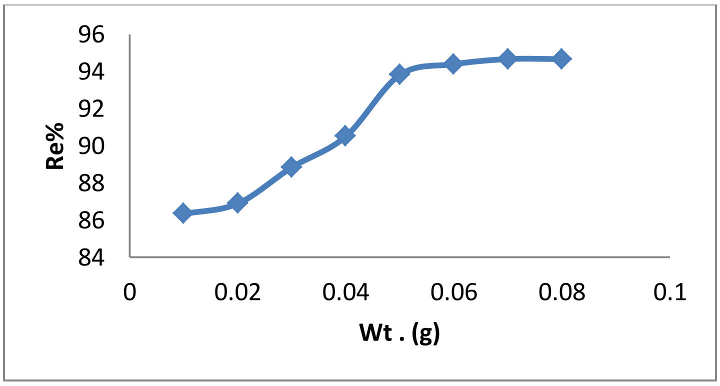


Figure 3: Effect of pH on the adsorption of: Remazol Brilliant Blue dye by Iraqi Porcelanite rocks. equilibrium time = 20 min , at 298 K.

Effect of Adsorbent Dos

Effect of adsorbent dose on removal Remazol Brilliant Blue dye is studied by varying the dose of adsorbent (0.01, 0.02, 0.03,0.04, 0.05 ,0.06 ,0.07 , and 0.08 g) in the test solution while keeping the initial dye concentration 40 mg L^{-1} at pH 6.7 and contact time 20mins at 298 K . As shown in (Figure 4). the percent of the adsorption increased with increasing adsorbent doses. The increase in the percent removal of dye with the increase in adsorbents dosage is due to the availability of larger surface area with more active functional groups[17]. Initially the rate of increase in the percent dye removal has been found to be rapid which slowed down as the dose increased. This phenomenon can be explained , based on the fact that at lower adsorbent dose the adsorbate (dye) is more easily accessible and because of this , removal per unit weight of adsorbent is higher. With rise in adsorbent dose, there is less commonsurate increase in adsorption, resulting from many sites remaining unsaturated during the adsorption.[17]. The result obtained indicate that the Porcelanite rocks has a large ential as an adsorbent for dye removal.



(Figure 4):**Effect of adsorbent dosage on the percentage removal of: Remazol Brilliant Blue dye by Iraqi Porcelanite rocks ., initial dye concentration= 40mg.L^{-1}, pH= 6.7 , and contact time (20 min)at 298 K.**

Adsorption Isotherm:

The general shape of the Remazol Brilliant Blue dye adsorption isotherm on the Porcelanite rocks are shown in Figure 5 and Table2, where the quantities of adsorbed on Porcelanite rocks (Qe) are plotted a function of equilibrium concentration (Ce) at (25, 35, 45 and 55)°C[18 ,19].

Table(2):Adsorption values of remazol brilliant blue dye from aqueous solution Iraqi Porcelanite rocks at different temperatures.

C_O ($mg.L^{-1}$)	298 K		308 K		318 K		328 K	
	C_e ($mg.L^{-1}$)	Q_e (mg/g)	C_e ($mg.L^{-1}$)	Q_e (mg/g)	C_e ($mg.L^{-1}$)	Q_e (mg/g)	C_e ($mg.L^{-1}$)	Q_e (mg/g)
10	0.577	3.926	0.8	3.833	1.911	3.37	2.355	3.185
20	1.466	7.722	1.8	7.583	2.8	7.166	3.133	7.027
30	1.911	11.703	2.355	11.518	3.355	11.102	3.688	10.963
40	2.244	15.731	2.688	15.546	3.466	15.222	4.022	14.99
50	2.911	19.6204	3.466	19.389	4.355	19.018	4.8	18.833
60	4.466	23.139	4.8	23	5.911	22.537	6.355	22.352

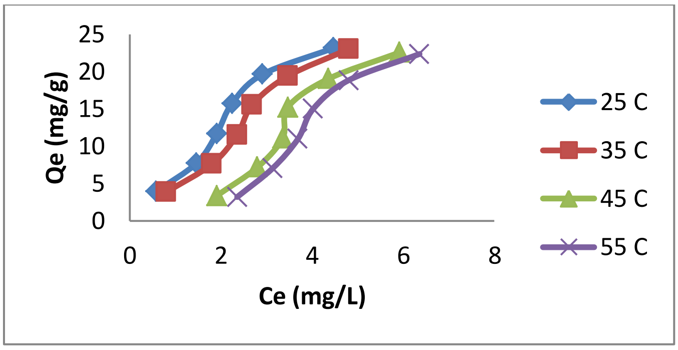


Figure. (5) : Adsorption Isothermof Remazol Brilliant Blue dye adsorption from aqueous solution on the surface of the the Iraqi Porcelanite rocks at different temperatures .

The shapes of the isotherms obtained from the experimental data were found to be comparable in all cases to the (S- curve) type according to Giles classification.The results obtained on the adsorption of Remazol Brilliant Blue were analyzed by the well-known models given by Langmuir and Freundlich.

Langmuir isotherm

The adsorption of Remazol Brilliant Blue at equilibrium with increase in initial dye concentration at 298-328 K has been fitted in Langmuir model and Freundlich isotherms.

The Langmuir isotherm is represented by the following equation:

$C_e/Q_e=1/ab+C_e/a$ ....(3)

Here Ce ($mg.L^{-1}$) is the equilibrium concentration of dye, Qe is the amount of dye adsorbed at equilibrium (mg.g-1).a and b are Langmuir constants related to the adsorption capacity and energy of adsorption respectively [20]. The values of a and b were determined from from slope and intercept of the plot Table (3).The essential features of Langmuir isotherm can be expressed in terms of dimensionless constant separation factor, RL that is calculated by the following equation to confirm the favourability of the adsorption process:

RL = 1 / (1 + bCo)......(4)

Where C0 is the initial dye concentration in solution (mg.L-1) and b is the Langmuir constant (Lmg-1). The value of RL indicates the type of the isotherm to be either favourable (0 < RL < 1), unfavourable (RL > 1), linear (RL = 1) or irreversible (RL = 0). The value of RL was found to be between 0.0043 and 0.2881 and confirm that the adsorption process is favorable.

Freundlich isotherm

Freundlich adsorption isotherm model used to explain the adsorption phenomenon is represented by the following equation:

$\text{Log } Q_e = \text{Log } K_f + 1/n \text{ Log } C_e$......(5)

Here Kf and n are constants incorporating all factors affecting the adsorption capacity and intensity of adsorption, respectively. The values of Kf and n were calculated from the intercept and slope of the plot. The magnitude of the exponent (n) gives an indication of the favourability and Kf the capacity of the adsorbent/adsorbate. The values of 1/n , less than unity is an indication that significant adsorption take place at low concentration but the increase in the amount adsorbed with concentration becomes less significant at higher concentration and vice versa [21].

The values of the regression coefficients indicate that the data satisfactorily follow both Langmuir and Freundlich models but the Freundlich isotherm the experimental data better.

Table(4): Langmuir and Freundlich parameters of adsorption isotherms at (298 – 328)K .

Adsorbate Remazol Brilliant Blue dye							
Temperatures	**Langmuir isotherm**				**Freundlich isotherm**		
	a (mg/g)	**b (mg/L)**	**Correlation coefficient (R^2)**	**RL**	**Intercept (Kf)**	**Slope (n)**	**Correlation coefficient (R^2)**
298 K	140.8450	0.0560	0.1767	0.3084	0.8074	0.9317	0.9644
308 K	-196.078	-0.0273	0.0925	-10.8695	0.6738	1.065	0.9734
318 K	-14.3266	-0.1681	0.537	-0.1746	0.0963	1.7679	0.9205
328 K	-10.0704	-0.1487	0.5566	0.2973	-0.1572	2.0246	0.9189

Effect of Temperature

The removal of Remazol Brilliant Blue dye using Iraqi Porcelanite rocks has been studied at 298 to 328 K. Determine the thermodynamic parameters, which is presented in (Figure. 6) Thermodynamic parameters, i.e. free energy (ΔG),enthalpy (ΔH) and entropy (ΔS) changes were also calculated using eqs.(6-9)[22] and are given in Table (5)

$\Delta G = -RT \ln K_{eq}$……………..…..(6)
$K_{eq} = (Q_e m)/C_e v$……………..……..(7)
$\ln K_{eq} = (-\Delta H/RT) + con.$ ....(8)
$\Delta S = (\Delta H - \Delta G)/T$ ………………. (9)

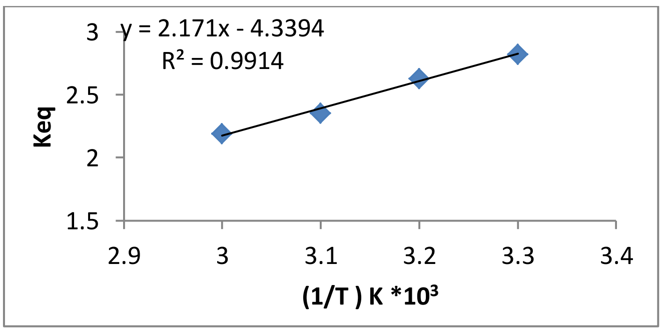


Figure.(6) Temperature dependence of the adsorption Remazol Brilliant Blue dye on the Iraqi Porcelanite rocks.

Table(5) Thermodynamic function ΔG,ΔS and ΔH of Remazol Brilliant Blue dye on the adsorbent surface Iraqi Porcelanite at (298-328)K.

Adsorbate Remazol Brilliant Blue			
Temperature	**ΔG(kJ/mol)**	**ΔH(kJ/mol)**	**ΔS (kJ/mol)**
298 K	-6.9917	-18.0496	-0.0371
308K	-6.7346	-18.0496	-0.0367
318K	-6.2262	-18.0496	-0.0371
328K	-5.9721	-18.0496	-0.0368

The negative values of the Gibbs energy indicated the spontaneous nature of the adsorption. The entropy was negative and the negative value of the enthalpy showed that the process is exothermic .

Conclusions :

The percent study shows that the Iraqi porcelanite rocks can be used as adsorbent for the removal of Remazol Brilliant Blued ye from aqueous solutions .The findings are: (1) The amount of dye adsorbed was found as function of initial pH, adsorbent dose, and contact time.(2) The adsorption equilibrium data were found to fit the Freundlich isotherm ,indicating a monolayer adsorption on a homogenous surface.(3) The negative ΔG values obtained from van 't Hoff plots confirm that the adsorptions of Remazol Brilliant Blue dye are spontaneous in nature and the negative ΔH values for the adsorption suggest that the adsorptions of Remazol Brilliant Blue dye on Iraqi Porcelanite rocks are exothermic in nature while the negative ΔS values indicates that the degrees of freedom decrease at the solid- liquid interface during adsorption of Remazol Brilliant Blue dye onto Iraqi Porcelanite rocks.

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