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RESEARCH ARTICLE

Effect of Modified Form of Porcelanite Rocks to Remove Remazol Brilliant Blue Dye From Aqueous Solution and Adsorption Isotherm Model Studies

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Abstract

The adsorption of Remazol Brilliant Blue dye from aqueous solutions by using (Porcelanite- Melamine-Urea) (PMUC) as an adsorbent .The characterization of (PMUC) was done by using FTIR spectroscopy, X-ray diffraction (XRD), (SEM) scanning electron microscopy and (AFM) Atomic force microscopy. Different experimental data such as contact time, pH, adsorbent dosage and ionic strength were studied. The equilibrium experimental data were analyzed by Langmuir, Freundlich and Temkin isotherm models. Thermodynamic parameters such as change in free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) were also determined.

Keywords: *Adsorption, Porcelanite rocks, Remazol Brilliant Blue, Isotherms, Langmuir, Freundlich, Temkin.*

Introduction

The industrial wastewater and pollutants water were required to the treatment to reused another time [1]. The treatment of industrial wastewater is carried out in various ways, in order to remove dyes, pigments, heavy metals, organic pollutants and other biological impurities [2]. A number of technologies have been developed over the years to remove various pollutants present in the water [3].

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 [4, 5].

Among these methods, adsorption is by far the most versatile and widely used method because of its low cost and eases of operation [2, 6]. Adsorption is more effective treatment process to remove chlorophenols from wastewater.

Different adsorbents, such as zeolite [7], sepiolite [8], bentonite [9], and carbon nano tubes [10] have been developed and their efficiency has been studied. Several studies have been carried out for removal RBB from aqueous solutions by Iraqi Porcelanite rocks [11]. And has been studied the removal of RBB from aqueous solutions by adsorption using Iraqi Porcelanite rocks and Modified Form.

The removal of RBB and MG from aqueous solutions by modified form seems to be more effective than unmodified samples [11, 12]. The Freundlich model was found to be fit for describing the equilibrium data The Iraqi porcelanite rocks represent one of the most and great adsorbents, because it is containing high percentage of silicon reached to 50% [13].

Experiments

Adsorbate and Adsorbent

The sorbate:- Remazol Brilliant Blue is water soluble which is used to colour the material like silk, wool, jute, leather, cotton, paper and other industries .dye (C. I. 61200) was obtained from M/s. Atul Industries, India.

Purity of dye was 50%. All the chemicals received were used without further purification [11].

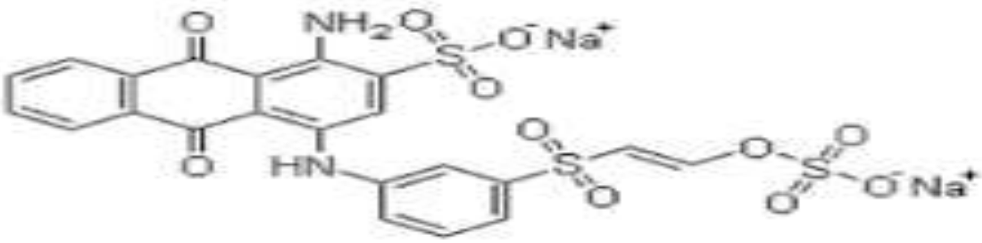

Figure 1: Chemical Structure of remazol Brilliant Blue dye

The adsorbent: - Preparation of Porcelanite-Melamine-Urea Complex (PMUC)

By mixing 1g from melamine with 1g from Porcelanite with 1g from urea in ceramic mortar and still about half an hour .Then transfer the mixture to the closed container and remained about [15] days in order to complete the distribution process of melamine molecules and urea molecules in porous of Porcelanite[15].The adsorption capacity of porcelanite is due to the large surface area within the composition of critobalite and tridymite [16, 17].

Characterization of the Modified Adsorbent

X-ray diffraction (XRD) Shimadzu 6000 powder diffractometer (Japan) using (CuKα radiation), (λ=1.5418A°) at 40kV and 30 mA and 2θ range of (5-80°). The Fourier transform infrared spectroscopy (FTIR) (Shimadzu) in the wave number range(4000-400cm^{-1}).The surface morphology of the samples was studied by using scanning electron microscope (SEM) type-T-Scan(Czech).The Atomic force microscopy (AFM)-spam AA3000, USA2008 (Shimadzu).

Adsorption Isotherm Studies

The experiments were carried out by shaking (0.02 g) of PMUC into conical glass flasks of (25mL) at various initial concentrations of the dye (10,20,30,40,50,60 and 70 mg/L) at different temperatures of (25,35,45 and 55 °C).

The experimental procedures for measuring adsorption equilibrium, adsorbent dosage, pH, Ionic strength and thermodynamics are described and discussed in our study. The concentration of remazol Brilliant Blue dye was determined by measuring the absorbance using Shimadzu UV-Vis 1800 digital double beam at a wavelength corresponding to the λ max. The adsorption capacity was calculated according to the equation (1).

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

Where Q_e is the adsorption capacity (mg/g); C_o is the initial remazol Brilliant Blue dye concentration (mg/L); C_e is the equilibrium remazol Brilliant Blue dye concentration (mg/L); V is the volume of the solution (L); and w is the mass of the adsorbent (g).The percentage of remazol Brilliant Blue dye removal was determined using the equation (2).

$$\%\text{Removal } (R\%) = \frac{(C_o - C_e)}{C_o} \times 100 \qquad (2)$$

Results and Discussion

FTIR Spectra

The FT-IR spectra of PMUC Figure 2 shows existence of the terminal silanol-OH and to the brighe Si-OH-Si .The band at (1600 cm^{-1}) could be attributed to the deformation of water molecules β(H_2O). The bands at (1157 cm-1) that appear as strong band can be assigned to ($\nu_{Si\text{-}O\text{-}Si}$) stretching viberations. The bands at (775cm^{-1}) are characteristic of Quartz and those at (464 cm^{-1}) can be attributed to β(Si-O-Si) bending vibrations [18]. Two sharp weaks band at the general range (3470-3132 cm^{-1}) attributed to asymmetric and symmetric stretching vibrations of (-NH_2) group and appearance of broad band at 3423 cm^{-1} due to the stretching vibration of hydroxyl group and other band at 3387 cm^{-1} belong to stretching vibration of (-N-H) band, [from this fact it can say that there is a reaction was been happened between two component melamine and urea [18]. The band at 1631 cm^{-1} attributed to bending vibration of (NH) group, while the two bands at 1550 and 1537 cm^{-1} assigned to stretching vibration of (C=N) inside melamine ring. The weak band at 1450 cm^{-1}

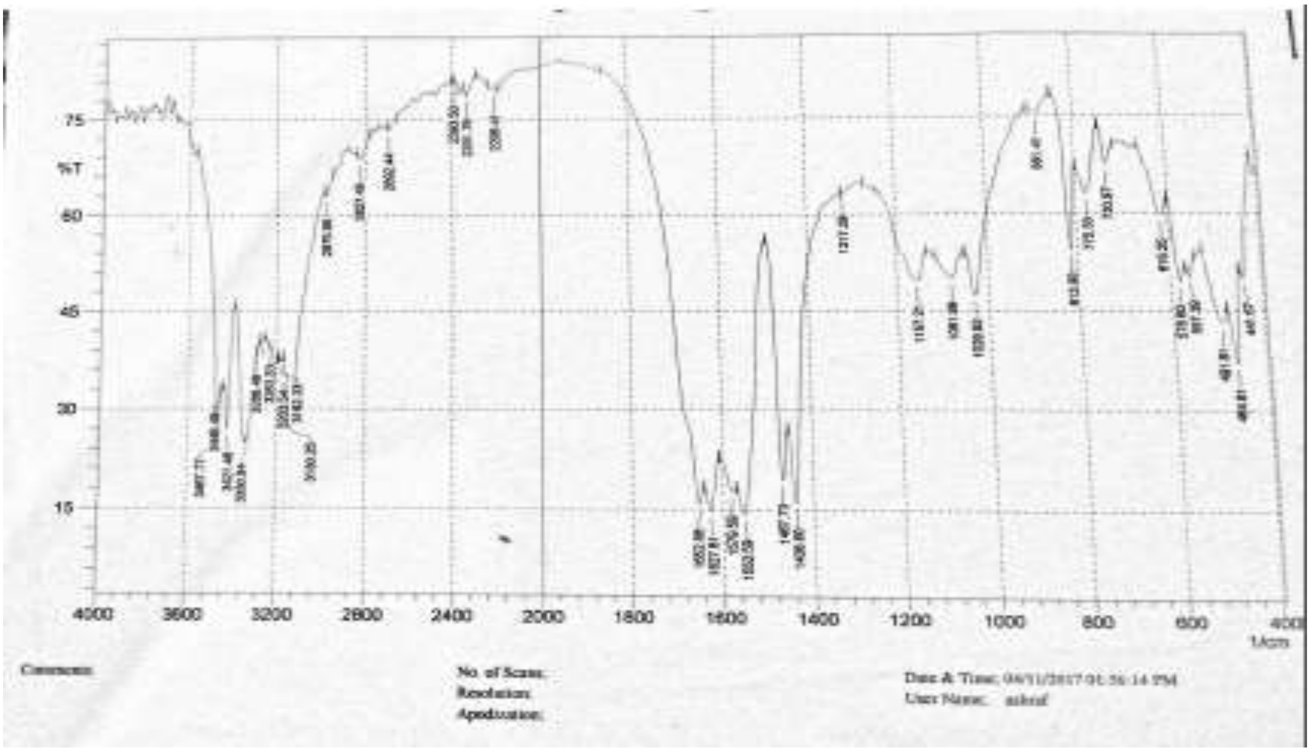

Figure 1: FTIR spectra of PMUC

SEM Analysis

The scanning electron microscopic demonstrates the crystalline structure, surface texture and porosity of Surface materials .The SEM micrograph of PMUC is shown in Figure 2. The micrograph of PMUC which presented in figure 2 indicated smooth surface with flat crystal.

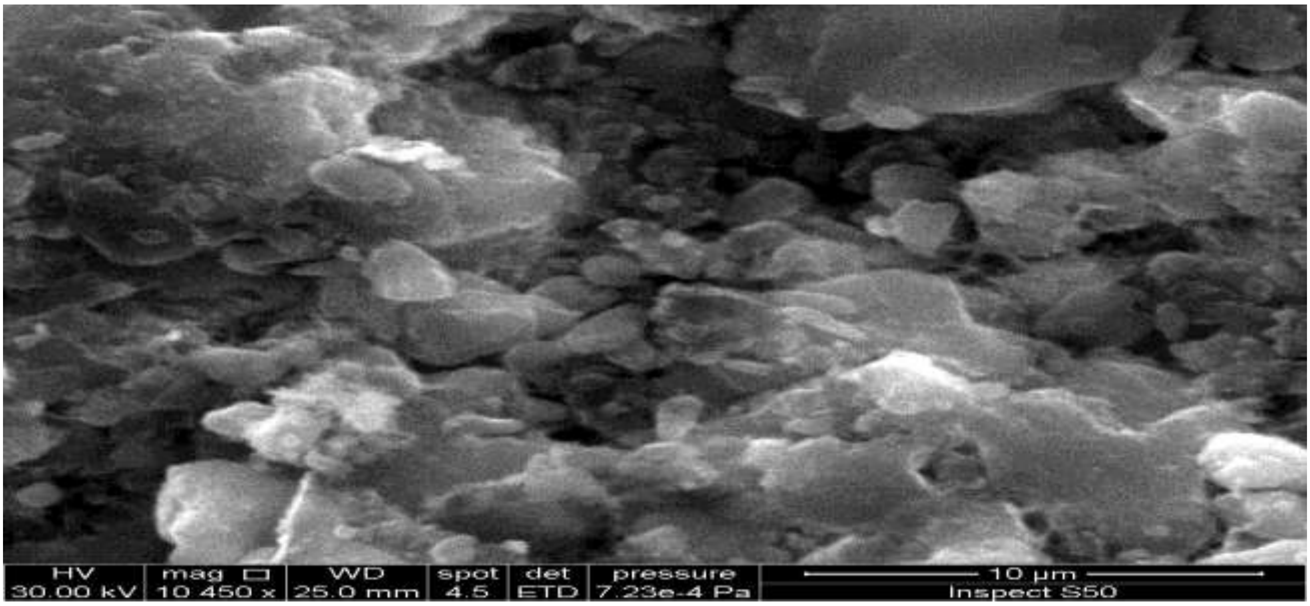

Figure 2: SEM photomicrograph of PMUC

XRD Analysis

The XRD spectrum of PMUC Figure 3 shows that the structure is maintained after modification because all peaks in modified form (PMUC) are broader and their intensities are lower when they are compared with that before modification that may indicate change in crystal size of the modified sample (PMUC). More especially, Scherre equation showed that the crystal size was reduced to nano-scale in PMFP.

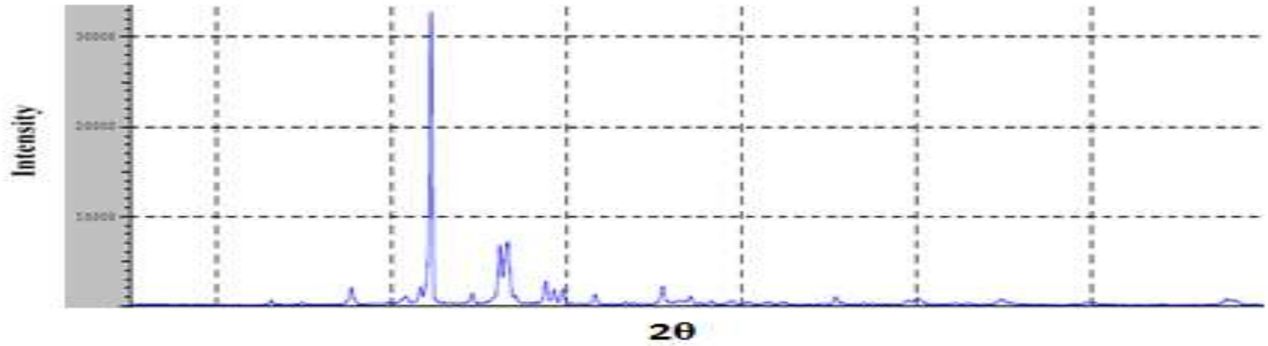

Figure 3: XRD analysis of the PMUC

Effect of Adsorbent Dosage

The effect of adsorbent dosage on the adsorption process of remazol Brilliant Blue dye by PMUC was studied at (25ºC) and initial concentration of (40 mg/L) as shown in Figure 4.

The figure indicates that sorption increased with increasing the sorbent dose up to 0.02g and then there was no further increase of sorption. The adsorption of the dyes increased rapidly with increase in the dose of the adsorbent due to greater availability of the exchangeable sites or surface area.

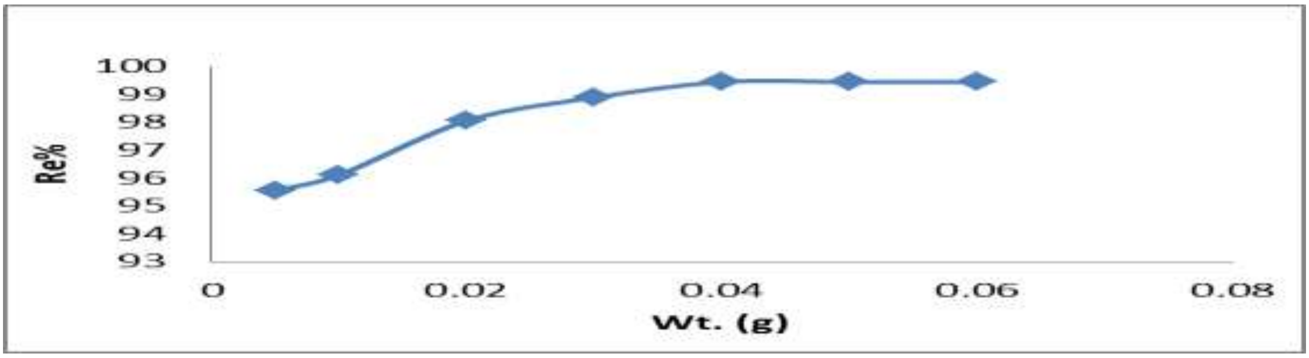

Figure 4: Effect of the adsorbent dosage on the adsorption of PMUC at 25ºC

Effect of Contact Time

Adsorption of remazol Brilliant Blue dye by PMUC was studied in an initial concentration of (40 mg/L) at 25º C .The time required to reach equilibrium was found to be (10 min.) for PMUC Figure 5.

The rapid adsorption observed at the initial stage was probably due to the abundant availability of binding sites on the adsorbent surfaces, after a certain period of time, at this moment, the adsorption capacity will remain constant due to the less active adsorption sites being available [19].

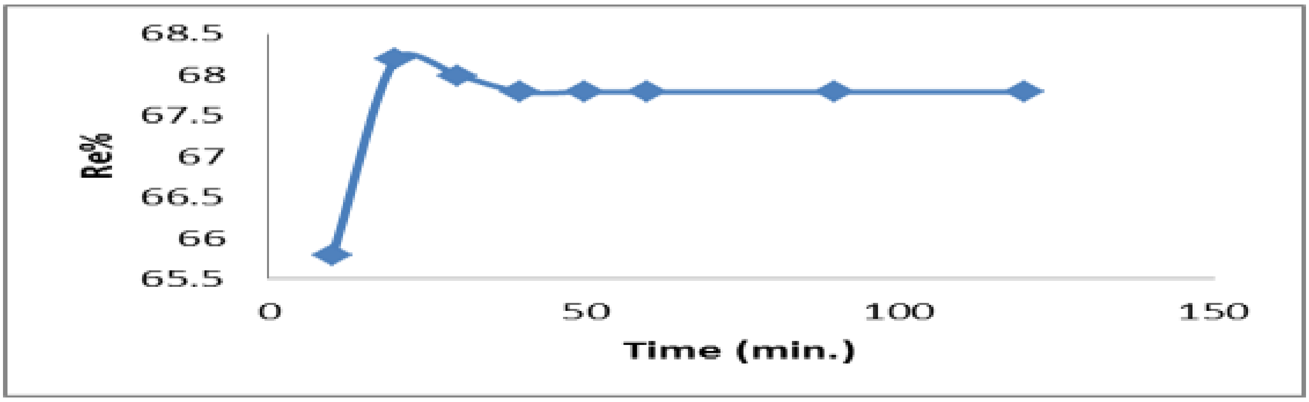

Figure 5: Effect of contact time on the adsorption of PMUC at 25ºC

Effect of PH

The effect of pH on the adsorption of remazol Brilliant Blue dye on PMUC was investigated at 25º C, initial concentration (40 mg/L) and adsorbent dosage (0.02 g). The desired pH was obtained by adding a few drops of (0.1 M) of NaOH and HCl. The results are shown in

Figure 6),), 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, PHS 6.7was selected for further experiments, and is 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 repultion 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 [20, 21].

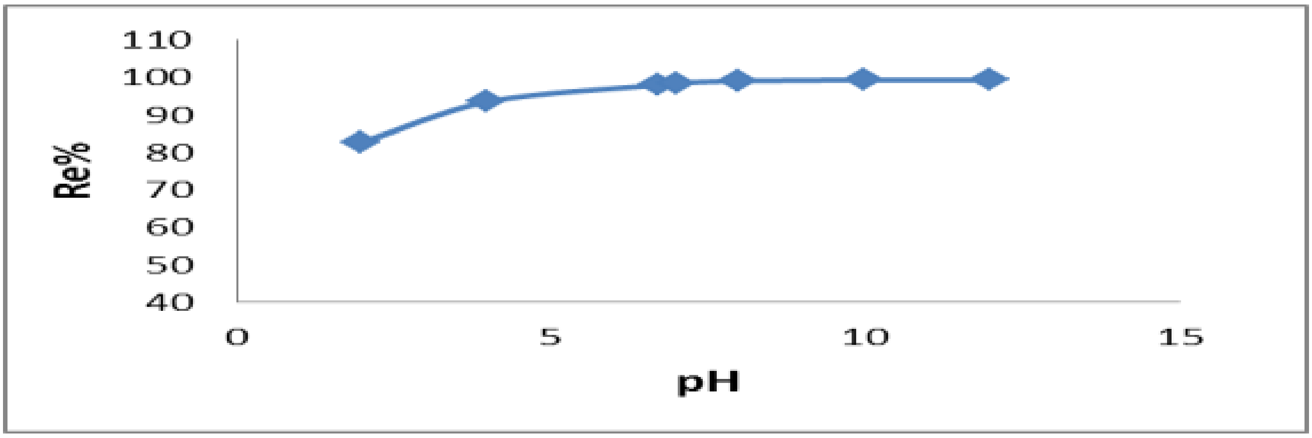

Figure 6: Effect of pH on the adsorption PMUC at 25°C

Effect of Ionic Strength

The effect of ionic strength on the adsorption ability was studied using NaCl, KCl, $MgCl_2$, $CaCl_2$ solution (0.02, 0.05, and 0.07M) and the concentration of remazol Brilliant Blue dye (40 mg/L) at pH (6.7) and temperature (25° C). The results of the study of the effect of ionic strength on remazol Brilliant Blue dye on the surface of PMUC indicate a decrease in adsorption capacity with increasing ionic intensity, which may be due to the higher solubility of salt solubility used in increasing ionic strength [21]. Makes the salt ions more competitive with the surface than the dye and thus reduces the adsorption capacity of the dye (Figure 7).The results of the study also indicate the difference in the effect of different salts used in the shipment and size on the dyes, where we observe the larger the ion and the larger the more interference in adsorption with remazol Brilliant Blue dye in the following order:

$Ca^{+2} > Mg^{+2} > K^{+1} > Na^{+1}$

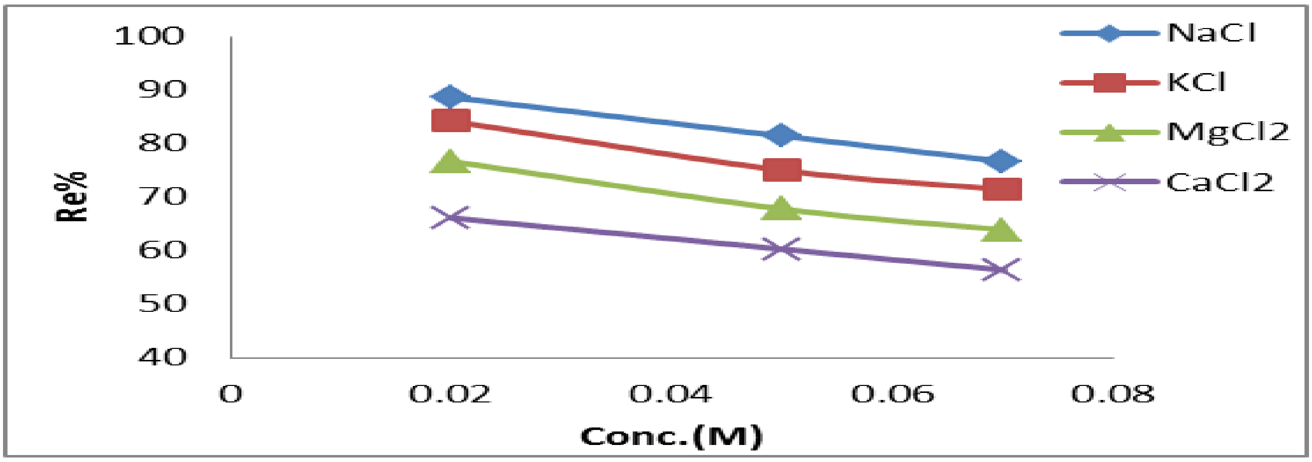

Figure 7: Effect of ionic strength on the adsorption of PMUC at 25°C and pH 8.5

Adsorption Isotherm

There are several adsorption isotherm models are used to describe the interaction behaviors between the adsorbent and adsorbate.

In this research, three isotherm models, namely: Langmuir, Freundlich and Temkin isotherm models were chosen to explain the mechanism of adsorption system [22].

The Langmuir isotherm is represented by the following equation:

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

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 is Langmuir constants related to the adsorption capacity and energy of adsorption respectively [23]. The values of a and b were determined from slope and intercept of the plot Table (1).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:

$$RL = 1 / (1 + b\ C_o) \ldots\ldots (4)$$

Where C_o 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 ($RL = 0$) [24]. The value of RL was found to be between 0.0043 and 0.2881 and confirm that the adsorption process is favourable.

Freundlich Isotherm

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

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

Here K_f and n are constants incorporating all factors affecting the adsorption capacity and intensity of adsorption, respectively. The values of K_f 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 K_f 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 [25].

The Temkin isotherm model assumes that heat of adsorption would decrease linearly with the surface coverage .The Temkin model can be expressed as in equation (6):

$$Q_e = B \ln K_T + B \ln C_e \qquad (6)$$

A plot of Q_e versus ln C_e enables the calculation of the constant K_T and B [26].

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

Table 1: Langmuir, Freundlich and Temkin models parameters of adsorption isotherms at (298 – 328) K

Adsorbate remazol Brilliant Blue dye										
Tem.	Langmuir isotherm				Freundlich isotherm			Temkin isotherm		
	a (mg/g)	b (mg/L)	(R^2)	RL	(Kf)	(n)	(R^2)	B	LnK_T	(R^2)
298 K	83.33	2.608	0.962	0.408	1.745	0.321	0.968	15.58	59.38	0.994
308 K	111.11	86.956	0.991	0.011	1.625	0.501	0.930	24.62	45.71	0.983
318 K	166.66	0.2608	0.807	0.7.11	1.457	0.656	0.860	32.28	26.72	0.954
328 K	250.00	0.104	0.580	0.811	1.322	0.800	0.903	40.74	10.73	0.966

Effect of Temperature

The removal of remazol Brilliant Blue dye using Iraqi PMUC 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.(7-9) [27] and are given in Table (2).

$$\Delta G = -RT \ln Keq \qquad \ldots\ldots\ldots\ldots\ldots\ldots (7)$$

$$Keq = (Q_e\, m)/C_e\, v \ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

$$\ln Keq=(-\Delta H/RT) + con. \quad (9)$$

$$\Delta S= (\Delta H - \Delta G)/T \quad (10)$$

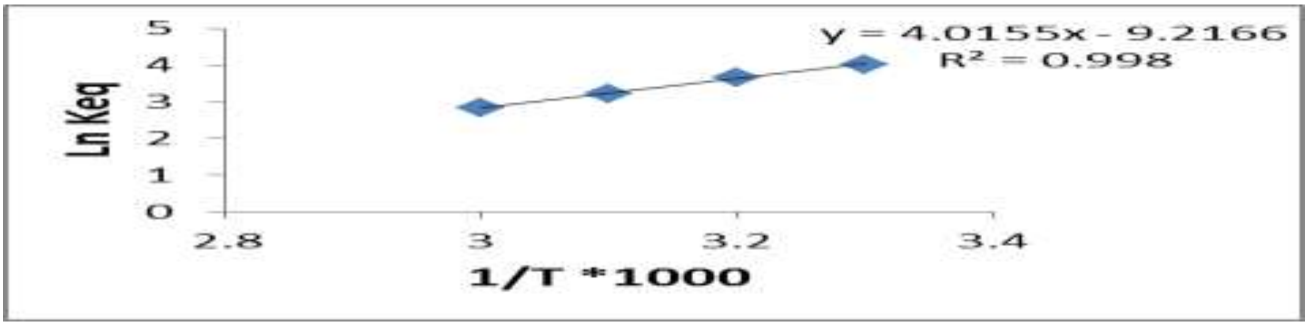

Figure 8: Temperature dependence of the adsorption remazol Brilliant Blue dye on the PMUC

Table 2: Thermodynamic function ΔG,ΔS and ΔH of remazol Brilliant Blue dye on the adsorbent surface PMUC at (298- 328)K

Adsorbate remazol Brilliant Blue dye			
Temperature	**ΔG(J/mol)**	**ΔH(J/mol)**	**ΔS (J/mol.K)**
298 K	-10.1122	-0.0333	0.0338
308 K	-9.3811	-0.0333	0.0303
318 K	-8.4859	-0.0333	0.0265
328 K	-7.7288	-0.0333	0.0234

It was found that the adsorption processes of Remazol Brilliant blue dye on PMUC were spontaneous and exothermic in nature from the negative values of ΔG and ΔH. The positive values of entropy when adsorption of dye over the temperature range characterize an increase disorder of the system and the driving force for adsorption is an entropy effect

Conclusions

A new surface (PMUC) adsorbent was synthesized to enhance adsorption of Remazol Brilliant blue dye from aqueous solution. The findings are: The amount of dye adsorbed was found as function of initial pH, adsorbent dose, and contact time the adsorption isotherm of Remazol Brilliant blue dye on PMUC was fitted with Temkin isotherm. The effect of temperature was investigated to calculate thermodynamic parameters. The analysis of these parameters explained that the process for Remazol Brilliant blue dye on PMUC was spontaneous and exothermic in nature while the positive ΔS values indicates that the degrees of freedom increase at the solid-liquid interface during adsorption of Remazol Brilliant blue dye onto PMUC.

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