Adsorption of a cationic dye (Yellow Basic 28) onto the calcined mussel shells:
Kinetics, Isotherm and Thermodynamic Parameters

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Abstract: The aim of this study is to valorise the mussel shells and evaluate the adsorption capacity of calcined mussel shells for the cationic dyes. The adsorbent was characterized by DRX, FTIR, BET and SEM, respectively. The adsorption of Yellow Basic28 on calcined mussel shells was investigated using the parameters such as concentrations (10-50mg/L), pH (3-10), ionic strength (0-2 mol / L) and temperature (288 - 318 °C). The adsorption rate data were analysed according to the first and second-order kinetic models. The adsorption kinetics was found to be best represented by the pseudo-second-order kinetic model. The experimental isotherm data were analyzed using Langmuir, Freundlich, Temkin, Elovich and Dubinin–Radushkevich isotherm equations on the dye-adsorbent system. The experimental data yielded excellent fits with Freundlich isotherm equation (R^2 = 0.966). It was indicative of the heterogeneity of the adsorption sites on the CMS particles. Various thermodynamic parameters such as enthalpy of adsorption $\Delta H°$, free energy change $\Delta G°$and entropy $\Delta S°$ were estimated. The positive value of $\Delta H°$(30.321 kJ/mol) and negative values of $\Delta G°$ (from -5.392 to -2.873 kJ/mol) show the process is endothermic and spontaneous. The negative value of entropy $\Delta S°$ (-87.172 J/mol K) suggest the decreased randomness at the solid-liquid interface during the adsorption of dyes onto calcined mussel shells.

Keywords: Calcined mussel shells, Yellow basic 28, Kinetic model, Adsorption isotherm, Thermodynamic parameters.

Introduction

Color effluents have been produced ever since the dyeing technique was invented. Various synthetic dyestuffs appeared in the effluents from various industries such as dyestuff, textiles, leather and paper[1]. So far, there are more than 100,000 types of dyes, with over 700,000 tonnes of dyestuff produced annually, which can be classified according to their structure as anionic and cationic[2]. The discharge of colored wastes into water not only affects the aesthetic nature but also interferes with transmission of sunlight into water[3], it is said that the presence less than 1mg L^{-1} some dyes in water is highly visible and undesirable[4]. In addition, dyes can cause severe damage to organism such as dysfunction of kidney, reproductive system, liver, brain and central nervous system[5]. Some dyes in wastewater are very difficult to treat using conventional wastewater treatment methods due to their complicated aromatic structures, hydrophilic nature and/or poor biological activity and they tend to pass through conventional treatment systems unaffected[6,7]. Therefore many other physiochemical methods are used for the removal of the dyes, such as including sonochemical degradation[8], chemical oxidation, coagulation/flocculation[9], photocatalytic decomposition[10], electro-catalytic degradation[11] and membrane filtration[12].

Recently, adsorption techniques have gained favor due to their simplicity in operation, cost-effectiveness, and efficiency in the removal of pollutants too stable for conventional methods[13,14]. Almost all the work related to adsorption techniques for colour removal from industrial effluents was based on studies using activated carbon. Other materials were also used as adsorbents for treating textile effluents. Activated carbon is still the most popular and widely used adsorbent but the main problem with its use is that it is a quite expensive adsorbent. Many researchers have been working diligently to find new adsorbents with a lower price,

such as aluminium magnesium mixed hydroxide[14], bentonite[15], zeolite[16], fly ash[17], activated sludge[18], agricultural residues[19], chitosan[20], ABM[21], clay minerals[22], sugarcane bagasse[23], Lignocellulosic[24-26], Clinoptilolite[27], Montmorillonite [28,30], Clay[31,32] and many other materials.

In this study we have studied the adsorption of cationic dye YB28 on mussel shells. The influence of several parameters (kinetics, contact time, sorbent amount, dye concentration, and pH) on the adsorption capacity was evaluated and discussed. The study of adsorption kinetics have been analyzed and the adsorption isotherm have been studied using various isotherms's models

Experimental Section

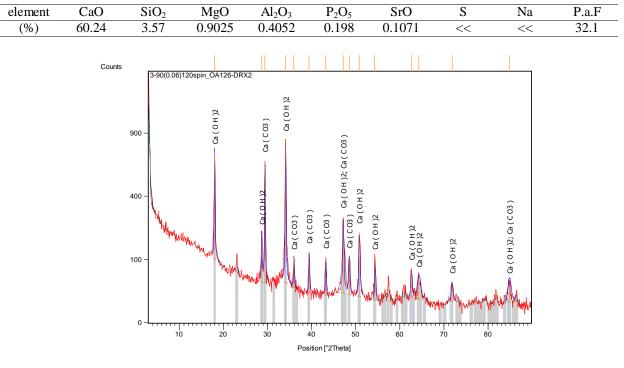### Preparation and characterization of calcined mussel shells adsorbent

The mussel shells used in this study were obtained from a popular restaurant in the city of Casablanca (Morocco). The mussel shells were washed several times with tap water and then were dried in an oven at 105 ℃ for 12 hours.

Mussel shells are dried and crushed to small grains calcined at 900 ℃ for 2 hours. The residue was washed with distilled water three times and after drying at 80 ℃ for 24 hours, the residue was finely chopped and ground into small particles of different sizes in the range of 75-100 microns (milled in an agate mortar) and washed with distilled water and dried overnight at 105 ℃ in a conventional oven and then calcined at a heating rate of 2 ℃ / min to 400 ℃ and maintained at this temperature for 4 hours. The resulting material was denominated the mussel shells calcined (CMS).

The final product is identified by X-ray diffraction (Philips X'Pert PRO), the analysis of IR spectroscopy (Bruker Tensor-27) and Elemental analysis. Elemental analysis (table 1)shows a high yield of Ca (60.24%) and Si (3.57%) compared to small amounts of Mg (0.90%), Al (0.41%), P (0. 20%) and Sr (0.11%). while the analysis by XRD showed the presence of calcite and portlandite, syn (Fig. 1).

Table 1. Elemental analysis of CMC

element	CaO	SiO$_2$	MgO	Al$_2$O$_3$	P$_2$O$_5$	SrO	S	Na	P.a.F
(%)	60.24	3.57	0.9025	0.4052	0.198	0.1071	<<	<<	32.1

Figure 1. DRX of CMS

The FT-IR spectrum of the CMS (Figure 2) indicates that the carbonate ion is present in CES. The substitution of the carbonate ion is identified by characteristic peaks around of $\upsilon_3 = 1400$ and $\upsilon_3 = 1465$, $\upsilon_2 = 874$ cm^{-1} and $\upsilon_4 = 713$ cm^{-1}, Broadband observed at $\upsilon_3 = 3448$ cm^{-1} indicates H$_2$O adsorbed in the samples. The band around $\upsilon_2 = 3640$ cm^{-1} is due to the OH group. The characteristic frequencies from PO_4^{3-} modes are observed at approximately $\upsilon_3 = 1127$ cm^{-1}, $\upsilon_3 = 551$cm^{-1} and $\upsilon_4 = 431$ cm^{-1}.
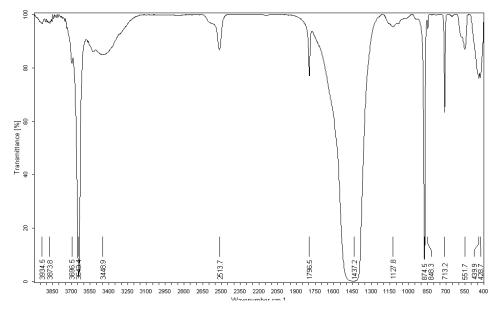
Figure 2. FT-IR spectra of CMS
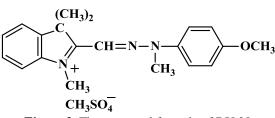
The dye

Figure 3. The structural formula of BY 28

The basic Yellow 28(BY 28) use in this studyis used in industry especially for dyeing and printing of polyacrylonitrile fiber, when ionized in aqueous solution, carries a positive charge and is named as a cationic dye, the structural formula of the dye is given in Fig. 3. Some physical properties[33,34] of this dye are summarized in Table 2.

Table 2: Physical properties of Basic Yellow 28 dye.

Dyeproperties	Basic Yellow 28
Commercial name	Maxilon Golden Yellow GL 200%
chemical formula	C21H27N3O5S
Molecularweight	433.52 g/mol
Solubility	90°C – 80 g/L 60°C – 60 g/L 30°C – 40 g/L
pH-stability	3-10
λ_{max}	438 nm
Type	Cationic

Methods

The effects of experimental parameters, pH (3-10), ionic strength (0-2 mol / L) and temperature (15, 25, 35 and 45 ° C) on the adsorption of dye have been studied in a batch mode of operation for a contact time of 270 min. The pH of the solution was adjusted adsorbate by addition of HCl (0.1 N) or NaOH (0.1 N) in solution. The samples of dyes were prepared by dissolving a known amount of dye in double distilled water and used as a stock solution and diluted to the required initial concentration. 100 ml of dye solutions were placed in a glass bottle. The solution is mixed continuously in a magnetic stirrer at a speed of 300 revolutions per minute. A given amount of CMS was dispersed in the dye solution. After a given contact time, 3 ml of mixture of the dispersion was taken, then the mixture was filtered and the absorbance of the filtrate was determined with a UV / visible spectrophotometer (6 BIOMATE, England), the dye concentration was calculated from a calibration curve.

The amount of dye adsorbed was determined by the difference between the initial concentrations and the remaining solution BY 28. The amount of adsorption q_t (mg/g) at time t was calculated by the following equation (2):

$$q_t = \frac{(C_o - C_t)V}{W} \quad (2)$$

Where, C_o and C_t (mg/L) are the liquid-phase concentrations of BY 28 at initial and any time t, respectively. V (L) is the volume of the solution, and W (g) is the mass of dry adsorbent used.

The absorbance value obtained in each case was then used to calculate the percentage biosorption of the dye on CES, by using the formula (3):

$$\% \text{ Biosorption} = \frac{(C_o - C_t)}{C_o} \times 100 \quad (3)$$

Where C_i and C_t are the initial and any time t absorbance values, respectively.

Results and Discussion

Effects of initial dye concentration and contact time

The initial concentration provides an important driving force to overcome all mass transfer resistances of all molecules between the aqueous and solid phases[35,36]. The initial concentrations of BY 28 solutions were changed and time intervals were assessed until no adsorption of adsorbate on CMS takes place. Fig. 4 shows the effects of contact time on the amount of BY 28 adsorbed by CMS under different initial dye concentrations. As shown in Fig 4, the adsorption increases with increasing initial BY 28 concentration. And the amount of dye removed at equilibrium increased from 3.21 to 22.34 mg/g with the increase in dye concentration from 10 to 50 mg/L. It is clear that the removal of dye depends on the concentration of the dye.
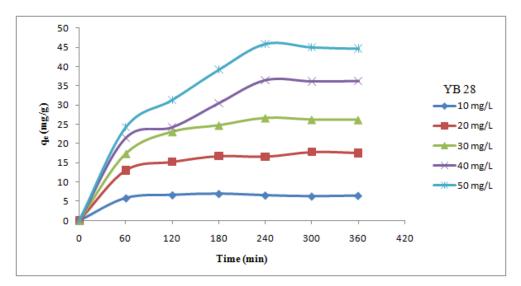

Figure 4. Effect of initial dye concentration on BY 28 adsorption (W = 1 g/L, T = 25°C, pH initial and Contact time = 6h)

The adsorption of BY 28 on CMS was also studied as a function of contact time in order to find out the equilibrium time for maximum adsorption. The results show that equilibrium time required for the adsorption of BY 28 on CMS for solutions with initial dye concentrations of 10-30 mg/L range from 120 to 150 min. However, more than 240min for BY 28 solutions within initial dye concentrations of 40-50mg/L. The samples were left for 360 min to ensure equilibrium.

Effect of initial pH on the adsorption of BY 28

The pH of the dye solution affects not only the surface charge of the adsorbent, the degree of ionization of the materials and the dissociation of functional groups on the active sites of the adsorbent,

but also the structure of the dye molecule[37]. The removal percentage of basic dyes by CMS at different pH values is plotted in Fig. 5. The removal percentage of BY 28 by CMS increased from 83.6% to 94.2% for an increase in pH from 3 to 10.

Several reasons may be attributed to the adsorption of dye by the CMS relative to pH. The surface of the CMS contains large number of reactive sites. At lower pH, the surface of the CMS gets positively charged thus making the H^+ ions compete effectively with dye cations causing decrease in the removal percentage. At higher pH, the surface of the CMS gets negatively charged, which enhances the interaction of positively charged dye cations with the surface of CMS through the electrostatic forces of attraction.
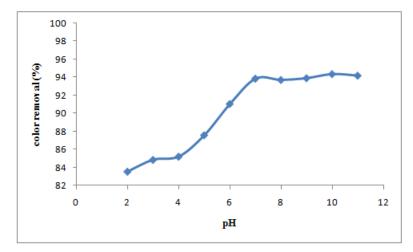
Figure 5. Effect of pH on BY 28 adsorption (W = 1 g/L, T = 25°C and contact time = 3h)

The effect of temperature on the adsorption of BY28

A study of the temperature dependence of adsorption process gives valuable information about the enthalpy during adsorption. The effect of temperature on the adsorption isotherm was studied by carrying out a series of isotherms at 15, 25, 35 and 45 °C as shown in Fig. 6.The adsorption capacity decreases with the increasing temperature.
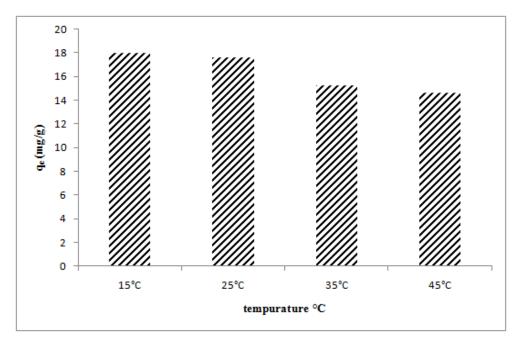

Figure 6. Effect of temperature on the adsorption of BY 28 on CMS (W = 1 g/L, pH initial and Contact time = 3h)

Adsorption kinetics

The study of adsorption kinetics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface. Adsorption rate constants for the basic dye were calculated by using pseudo-first order, second-order[38,39] which were used to describe the mechanism of the dye adsorption. The conformity between the experimental data and the model-predicted values was expressed by the correlation coefficients (R^2). A relatively high R^2 value indicates that the model successfully describes the kinetics of the dye adsorption.

The pseudo-first-order equation

The pseudo-first-order equation can be expressed in a linear form as [40]:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \qquad (4)$$

where q_e and q_t are the amount of dye adsorbed (mg/g) on the adsorbents at the equilibrium and at time t, respectively, and k_1 is the rate constant of adsorption (min^{-1}). Values of k_1 and the correlation coefficients (R^2) were calculated from the plots of $\ln(q_e-q_t)$ versus t. It was found that the Application of

the first-order kinetic model to the present experimental data gave a poor fit, The R^2 values under different conditions were calculated and listed in Table 3, so it is clearly that of the first-order kinetic model is not appropriate for the BY 28/CMS system.

Table 3. Kinetic parameters for the removal of BY 28 by CMS

[NaCl] (mol/L)	pH	T (°C)	$q_{e,exp}$ (mg/g)	First-order kinetic model			Second-order kinetic model		
				K_1 (1/min)	$q_{e,cal}$ (mg/g)	R^2	K_2 (g/mg.min)	$q_{e,cal}$ (mg/g)	R^2
-	3	-	18.373	0.0221	9.323	0.889	0.0052	19.231	0.999
-	5	-	17.52	0.0216	10.229	0.879	0.0036	19.048	0.998
-	7	-	18.775	0.0315	13.886	0.871	0.0046	19.646	0.996
-	9	-	17.458	0.0125	7.211	0.584	0.0037	18.868	0.990
	11		17.999	0.0125	13.680	0.584	0.0046	19.014	0.998
0.2	-	-	16.891	0.0257	5.369	0.828	0.0052	18.868	0.998
0.4	-	-	17.523	0.0128	4.134	0.586	0.0059	18.382	0.995
0.6	-		18.224	0.0120	2.068	0.233	0.0184	17.065	0.999
-	-	15	18.553	0.0366	10.642	0.8783	0.0093	18.553	0.999
-	-	25	17.212	0.0239	7.576	0.8128	0.0457	17.212	0.998
-	-	35	18.315	0.0174	15.156	0.8305	0.0012	18.315	0.928
-	-	45	16.420	0.0209	11.201	0.8354	0.0032	16.420	0.995

C (BY 28) = 20 mg/L

The pseudo-second-order equation

The pseudo-second-order kinetic model can be represented in the following form [41]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_{e2}} + \frac{t}{q_e} \qquad (5)$$

Where q_e is the amount of dye adsorbed at equilibrium (mg/g) and k_2 is the rate constant of pseudo-second-order adsorption (g/mg min). The values of k_2 and q_e can be determined experimentally from the slope and intercept of plot t/q_t versus t. The k_2 and q_e values under different conditions were calculated and listed in Table 3

The linear plots of t/q_t versus t show good agreement between experimental ($q_{e(exp)}$) and calculated ($q_{e(cal)}$) values (Table 3). Also the correlation coefficients for the second-order kinetics model (R^2) are greater than 0.99, indicating the applicability of this kinetic equation and the second

order nature of the adsorption process of BY28 onto CMS and the process is chemisorptions controlled[42].

Equilibrium isotherm

In order to optimize the design of an adsorption system to remove dye from solutions, it is important to establish the most appropriate correlation for the equilibrium curve. Adsorption equilibrium is established when the amount of dye being adsorbed onto the adsorbent is equal to the amount being desorbed. It is possible to depict the equilibrium adsorption isotherms by plotting the concentration of the dye in the solid phase versus that in the liquid phase. Several isotherms models can be used to describe the equilibrium of adsorption. Five common isotherm equations were tested in the present study: Langmuir[43], Freundlich[44], Temkin[45], Elovich.[46] and Dubinin-Radushkevich[47] The models used are shown in Table 4.
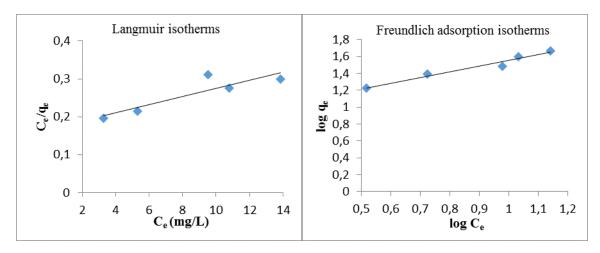
Table 4. Isotherm models tested in this study

Isotherm	Nonlinear form	Linear form	plot
langmuir	$\dfrac{q_e}{q_m} = \dfrac{K_L C_e}{1+K_L C_e}$	$\dfrac{C_e}{q_e} = \dfrac{1}{q_m\,K_L} + \dfrac{C_e}{q_m}$	$\dfrac{C_e}{q_e}$ vs. C_e
Freundlich	$q_e = K_F C_e^{\,n}$	$\log(q_e) = \log(K_F) + n\log(C_e)$	$\log(q_e)$ vs. $\log(C_e)$
Elovich	$\dfrac{q_e}{q_m} = K_E C_e \exp\!\left(-\dfrac{q_e}{q_m}\right)$	$ln\dfrac{q_e}{q_m} = \ln(K_E C_e - \dfrac{q_e}{q_m}$	$ln\dfrac{q_e}{q_m}$ $vs.\ q_e$
Temkin	$\dfrac{q_e}{q_m} = \dfrac{RT}{\Delta Q}\ln(K_T C_e)$	$q_e = B_T \ln K_T + B_T \ln C_e$ (with $B_T = \dfrac{q_m RT}{\Delta Q}$)	q_e vs. $\ln C_e$
Dubinin-Radushkevich	$q_e = q_m \exp(-\beta\varepsilon^2)$ (with $\varepsilon = RT\ln(1 + \dfrac{1}{q_e})$	$\ln(q_e) = \ln(q_m) - \beta\varepsilon^2$	$\ln(q_e)$ vs ε^2

The application of the langmuir, Elovich and Dubinin–Radushkevich models to the present experimental data gave a poor fit (Fig. 7), however, so that it is clearly not appropriate for the BY 28/CMS system. While the application of the Freundlich and Temkin isotherm model (Fig. 7) show a good regression coefficient compared to tree model before cited (Table 5).

Table 5. Isotherm parameters for BY 28 adsorption onto CMS

Isotherm model	Parameters		
Langmuir	$q_m = 93.458$ mg/g	$K_L = 0.064$ mg/g	$R^2 = 0.787$
Freundlich	$K_F = 2.415$ mg^{1-n} L^n /g	$n = 0.671$	$R^2 = 0.966$
Temkin	$K_T = 0.684$ L/mg	$B_T = 19.124$	$R^2 = 0.925$
Elovich	$q_m = 69.444$ mg/g	$K_E = 0.089$	$R^2 = 0.661$
Dubinin-Radushkevich	$q_m = 41.388$ mg/g	$\beta = 2\ 10^{-6}$	$R^2 = 0.879$

Examination of the linear isotherm plots suggested that the Freundlich model yielded a much better fit than the other models, which indicates multilayer adsorption with interaction between adsorbed molecules and also the heterogeneous distribution of active sites on the material, since the model presupposes that the surface is heterogeneous[44].
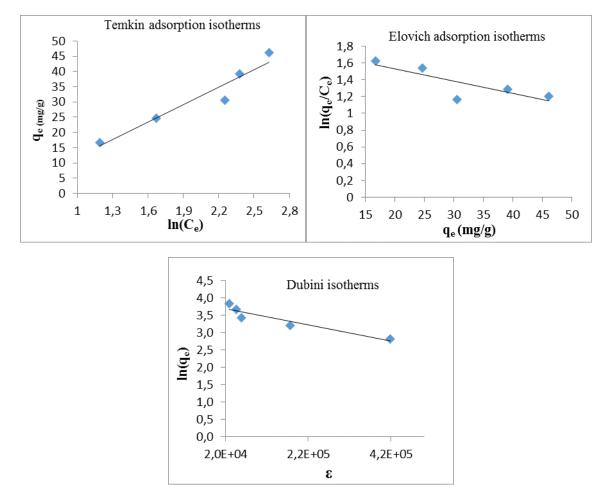
Figure 7. Linear form of isotherm models tested in this studyof BY 28 onto CMS.

Thermodynamic studies

The thermodynamic parameters including Gibbs free energy change ($\Delta G°$), enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) were calculated from the following equations[48-49];

$$\Delta G° = -RT \, LnK_L \quad (10)$$

Where R is the universal gas constant (8.314 J/mol K), T is the temperature (K) and K_L value was calculated using the following equations:

$$K_L = \frac{q_e}{C_e} \quad (11)$$

Where q_e (mg/g) and C_e (mg/L) are the equilibrium concentration of BY 28 ions on CMS and in the solution, respectively.

The enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) of the adsorption were estimated from the following equation:

$$Ln \, K_L = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \quad (12)$$

The enthalpy ($\Delta H°$) and entropy ($\Delta S°$) can be obtained from the slope and intercept of $Ln \, K_L$ versus 1/T.

$$\Delta G° = \Delta H° - T\Delta S° \quad (13)$$

Where $\Delta G°$ is the Gibbs free energy change (J), R the universal gas constant (8.314 J/mol K) and T is the absolute temperature (K).

By plotting a graph of $ln(K_L)$ versus 1/T (fig 8) the values $\Delta H°$ and $\Delta S°$ can be estimated from the slopes and intercepts.

The negative values of $\Delta G°$ at different temperatures indicate the feasibility of the process and the spontaneous nature of the process of elimination dye on CMS. Generally, the change in adsorption enthalpy for physicsorption is in the range of -20 to 40 kJ/mol, but chemisorption is between -400 and -80 kJ/mol. The positive $\Delta H°$ (30.321 kJ/mol) reveals the process is endothermic and physical in nature. Furthermore, the negative values of $\Delta S°$ (-87.172 j/mol K) suggest the decreased randomness at the solid-solution interface during the process of elimination dye on CMS.

Table 6. Thermodynamic parameters for the adsorption of BY28 onto CMS

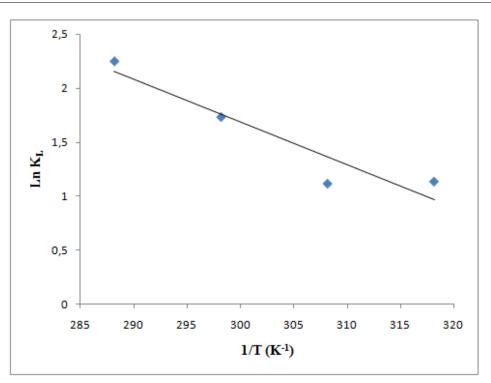| Temperature(K)	Thermodynamic parameters		
	$\Delta G°$(kJ/mol)	$\Delta H°$(kJ/mol)	$\Delta S°$(J/mol K)
288.15	-5.392		
298.15	-4.303	30.321	-87.172
308.15	-2.873		
318.15	-3.016		

Figure 8. Plot of lnK_L vs. 1/T for estimation of thermodynamic parameters for the adsorption of BY 28 onto CMS

Conclusion

The present study shows that the CMS can be used as a potential adsorbent for the removal of BY 28 from the aqueous solution. The results showed the adsorption increases with increasing initial BY 28 concentration. And the amount of dye removed at equilibrium increased from 3.21 to 22.34 mg/g with the increase in dye concentration from 10 to 50 mg/L. The removal percentage of BY 28 by CMS increased from 83.6% to 94.2% for an increase in pH from 3 to 10. The adsorption capacity decreases from 17.97 to 14.62 mg/g with the increasing temperature from 288 to 318 ℃ respectively.

The experimental results have shown that the adsorption rate could be considered to be pseudo-second order $R^2 > 0.995$ at different condition of pH, temperature and Sodium chloride's concentration. The adsorption isotherm data were analyzed by the Langmuir, Freundlich, Temkin, Elovich and Dubinin-Radushkevich models using linear regression, the best fit to the data was obtained with the Freundlich isotherm models ($R^2 = 0.966$) which indicates the multilayer adsorption and the heterogeneous distribution of active sites on the material.

The positive value of $\Delta H°$ (30.321 kJ/mol) and negative values of $\Delta G°$ (from -5.392 to -2.873 kJ/mol) show the sorption process is endothermic and spontaneous. The negative value of entropy $\Delta S°$ (-87.172 J/mol K) shows the decreased randomness at the solid-liquid interface during the process of elimination dye on CMS.

The results indicate that CMS could be employed as low-cost alternatives to the commercially available adsorbents in wastewater treatment for the removal of cationic dyes

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