



Adsorption of malachite green on silica gel: Effects of NaCl, pH and 2-propanol

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ABSTRACT

Adsorption of malachite green (MG) on silica gel was studied as a function of temperature (308–328 K), pH, different concentrations of NaCl and various weight percentages of binary mixtures of 2-propanol with water. It was observed that the adsorption capacity decreases with increase in weight percentage of 2-propanol and NaCl and HCl concentration compared to that of in water. Results showed that in the presence of 2-propanol, surface aggregates of MG form on silica gel due to aggregation of MG molecules in these solutions, reverse desorption occurs. Binding constants of MG to silica gel were calculated using the Langmuir and bilayer isotherms. The process is exothermic in water and endothermic in NaCl solutions. The mean adsorption energy (E) value 9.0–14.2 kJ mol⁻¹ indicated chemical adsorption.

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1. Introduction

Dyes are important pollutants, causing environmental and health problems to human being and aquatic animals. Malachite green (MG), a basic dye, is most widely used for coloring purpose, amongst all other dyes of its category [1] and its molecular structure is shown in Fig. 1. MG is most commonly used for the dyeing of cotton, silk, paper, leather and also in manufacturing of paints and printing inks. It is a toxic chemical and largely used to treat parasites, fungal infections, and bacterial infections in fish and fish eggs [2].

Despite its extensive use, MG is a highly controversial compound due to its reported toxic properties which are known to cause carcinogenesis, mutagenesis, teratogenesis, and respiratory toxicity [3]. Most of dyes, including MG, are toxic and must be removed before discharge into receiving systems to prevent environmental pollution. Adsorption methods employing solid adsorbents are widely used to remove certain classes of chemical pollutants from wastewater [4–9]. Some adsorbents, such as chitosan [10], activated carbon [11], soil, ground shrimp skeleton, ground oyster

Shell, ground charcoal [12], TriSyl silicas [13], de-oiled soya [14] and microalgae [15] were used to remove MG from industrial wastewater.

Silica gel is a hydrophilic porous adsorbent. Aromatic compounds are found to involve the pi-cloud in hydrogen bonding with silanol (SiOH) group during adsorption. Cationic and nonionic

surfactants adsorb on silica surface involving hydrogen bonding [16]. As previously reported, styryl pyridinium dyes adsorb on silica surface [17,18]. Organic cosolvents [19], ionic strength and pH value of solution [10,20,21] can affect on the adsorption capacity of adsorbents.

In this work, we studied effects of temperature, NaCl, pH and 2-propanol on adsorption of malachite green on silica gel.

2. Materials and methods

Malachite green oxalate, NaCl, HCl, silica gel 60 for column chromatography (mean pore diameter 60 Å) and 2-propanol (≥99%) were purchased from Merck.

Ten ml of MG solution of different initial concentrations was transferred to a series of 15-ml glass stoppered bottles, each containing 0.035 g of silica gel sample. The solutions were shaken at 120 rpm in a temperature controlled shaking water bath (Fater electronic Co., Persian Gulf model) at 308, 318 and 328 K within ±0.1 K for 20 h to reach equilibrium under experimental conditions.

The initial concentrations of MG were up to 6.3×10^{-5} M. After adsorption, the contents of MG in the residual solutions were determined by spectrometry (UV–vis 160, Shimadzu) at its λ_{\max} values in these solutions which are around the λ_{\max} value of MG in water, 620 nm. The adsorption capacity of MG on the adsorbent, q_e (mg g⁻¹), was calculated by a mass balance relation as follows

$$q_e = \frac{(c_0 - c_e)Mv}{1000w} \quad (1)$$

where c_0 and c_e are the initial and equilibrium concentrations of adsorbate (M) respectively, v is the volume of solution (ml), w is

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Table 1
Parameters obtained from the Temkin, Langmuir and Dubinin–Radushkevich isotherms for adsorption of MG on silica gel in different concentrations of NaCl at 308–328 K.

[NaCl] (M)	Temkin			Langmuir			Dubinin–Radushkevich		
	c_1	c_2	R^2	K	q_{mon}	R^2	$\ln q_D$	E	R^2
T = 308 K									
0.0	1.866	7354517	0.990	774194	8.3	0.994	4.598	13.5	0.988
0.07	0.993	644762	0.996	74286	4.3	0.998	3.563	12.0	0.986
0.1	0.770	872590	0.994	98052	3.3	0.998	3.558	11.7	0.991
0.3	1.198	366965	0.987	41648	5.2	0.986	3.718	11.5	0.976
0.7	1.744	257571	0.990	29812	7.9	0.978	4.397	10.7	0.978
2.0	–	–	–	–	–	–	7.882	11.5	0.981
T = 318 K									
0.0	1.817	5952605	0.982	596939	8.5	0.979	5.530	12.3	0.974
0.07	0.825	811030	0.990	85535	3.7	0.999	3.931	11.6	0.989
0.1	0.646	1173184	0.992	139689	2.8	0.994	2.895	13.6	0.986
0.3	0.643	1023008	0.985	120530	2.7	0.993	2.822	13.7	0.975
0.7	1.248	310716	0.985	34972	5.4	0.999	4.205	10.9	0.994
2.0	–	–	–	1132	142.2	0.997	6.236	9.0	0.987
T = 328 K									
0.0	2.005	4543359	0.984	437500	9.5	0.992	4.874	13.6	0.992
0.07	0.772	963664	0.987	91667	3.6	0.994	3.590	12.6	0.962
0.1	1.063	1701687	0.985	211881	4.7	0.997	3.452	14.2	0.986
0.3	0.640	1352124	0.998	146694	2.8	0.996	3.063	13.6	0.984
0.7	1.102	327332	0.991	37722	4.7	0.991	3.992	11.5	0.993
2.0	–	–	–	11840	12.2	0.998	5.550	9.7	0.994

Dimension of c_1 , q_{mon} and q_D is mg g^{-1} . Dimensions of c_2 , K and E are in M^{-1} , M^{-1} and kJ mol^{-1} , respectively. Data of adsorption of MG on silica gel in 2 M NaCl at 308 K satisfy the Freundlich isotherm and the related parameters are $\log K_F = 6.29$, $n = 0.847$ and $R^2 = 0.992$.

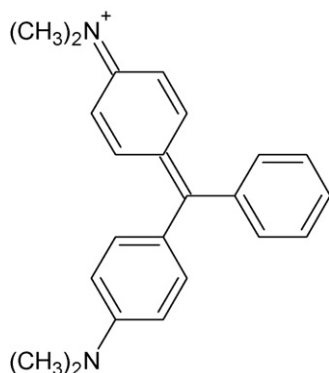


Fig. 1. Molecular structure of MG.

the weight of the used adsorbent (g) and M is the molecular weight of adsorbate (g).

The relation between q_e (mg g^{-1}) and c_e (M) has been studied by the Freundlich [22,23], Temkin [24], Langmuir [25] and Dubinin–Radushkevich equations [26–29] which are explained in Supplementary data.

In the last part of this work, the results are studied by “*adsorption isotherm regional analysis model*” or abbreviated as ARIAN model [30]. This model is introduced for studying adsorption isotherms up to four regions. In ARIAN model which is explained briefly, it is assumed that:

(A) Depending on the used concentration range, different interactions may occur between adsorbate and adsorbent. The

concentration range related to each kind of interactions is called a “*region*” and data of various regions are interpreted by different adsorption isotherms.

- (B) In each region, the adsorbate concentration range that satisfies locally in an adsorption isotherm or small plateau, is called a “*section*”. A region may include one or more sections. The sections would be symbolized by large English alphabets.
- (C) Region 1 obeys Henry’s law.
- (D) Region 2 includes only formation of monolayer surface aggregates and can be studied by an appropriate isotherm.
- (E) In region 3, new surface aggregates form. The concentration in which region 3 starts, is called the *starting third region concentration* (abbreviated as stc). Data of region 3 are analyzed by the bilayer equation, Eq. (2), and its derived ones, Eqs. (3) and (4), and equilibrium constants of monolayer and/or bilayer adsorption of adsorbate molecules are obtained.
- (F) Region 4 starts from maximum adsorption capacity, q_{max} . The surfactant concentration corresponding to maximum adsorption capacity, q_{max} , symbolized by c_{max} . This region is studied by the reverse desorption equation, Eq. (5), whether it is as plateau or curve goes down.

In the third region, assuming adsorption occurs mostly in the first and second layer, we have

$$\frac{c_e}{q_e} = \frac{1 + c_e K_{\text{sa}} + x c_e^2 K_{\text{sa}}}{q_{\text{mon}} K_{\text{sa}} + 2 q_{\text{mon}} x c_e K_{\text{sa}}} \quad (2)$$

where q_{mon} and q_e are the monolayer and equilibrium adsorption capacity, respectively. K_{sa} and x are the adsorption equilibrium constants of adsorbate molecules in surface aggregates and in all layers

Table 2
 ΔH and ΔS values of the second region of adsorption of MG on silica gel from water and in the presence of various concentrations of HCl and NaCl at 308–328 K.

System	ΔH	ΔS	System	ΔH	ΔS
Water	–23.9	34.9	NaCl (0.7 M)	9.9	118.1
NaCl (0.07 M)	8.9	122.2	NaCl (2.0 M)	Endothermic	
NaCl (0.1 M)	32.3	200.4	HCl (0.0006 M)	–77.0	–132.2
NaCl (0.3 M)	53.2	262.7	HCl (0.005 M)	68.0	–296.5

ΔH and ΔS values are in kJ mol^{-1} and $\text{J mol}^{-1} \text{K}^{-1}$, respectively.

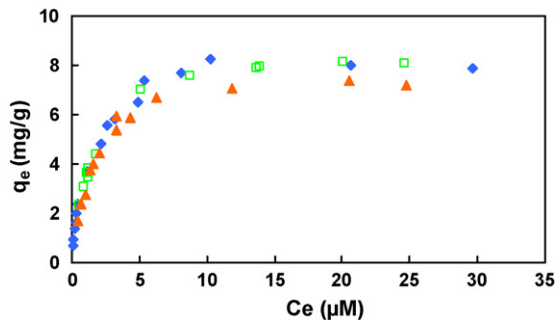


Fig. 2. Variation of q_e vs. c_e for adsorption of MG on silica gel from water at \blacklozenge 308, \square 318 and \blacktriangle 328 K.

above first one, respectively. Eq. (2) is called “bilayer isotherm”. If adsorbate molecules adsorb mostly on the first layer, Eq. (2) can be written as

$$\frac{c_e}{q_e} = \frac{1}{q_{\text{mon}}K_{\text{sa}}} + \frac{c_e}{q_{\text{mon}}} + \frac{xc_e^2}{q_{\text{mon}}} \quad (3)$$

which is used for low bilayer coverage (abbreviated as LBC). On the other hand, if the adsorption process is monolayer, Eq. (2) can be reduced to

$$\frac{c_e}{q_e} = \frac{1}{q_{\text{mon}}K_{\text{sa}}} + \frac{c_e}{q_{\text{mon}}} \quad (4)$$

where Eq. (4) is a Langmuir-type equation. Reverse desorption isotherm is as follows

$$q_e = q_{\text{srd}} \exp\{-k_{\text{rd}}(c_e - \text{srd})\} \quad (5)$$

where k_{rd} is the reverse desorption constant and q_{srd} is the equilibrium adsorption capacity at srd [30]. Concentration in which the reverse desorption starts, is called “starting reverse desorption concentration” (abbreviated as srd) and several srd may be observed in region 4. It is assumed that at srd , new micellar structure forms in solution. If $k_{\text{rd}} = 0$, region 4 is as plateau.

3. Results and discussion

3.1. Adsorption of MG on silica gel

Fig. 2 shows the adsorption isotherms of MG on silica gel at 308–328 K. Binding constants of MG to silica gel were calculated using the Langmuir and Temkin isotherms and the related thermodynamic parameters were obtained. The results show that q_{mon} value increases with increase in temperature, Table 1 and adsorption is exothermic and its ΔS value is positive, Table 2.

The mean adsorption energy (E) value, obtained from the Dubinin–Radushkevich equation, is between 12.3 and 13.6 kJ mol^{-1} at different temperatures which indicates that MG molecules are adsorbed chemically on silica gel, Table 2. It seems that adsorption process occurs through interaction between MG and oxygen atom of silanol group of silica gel. As previously reported, adsorption of MG onto chitosan occurs through interaction between MG and pair electrons of nitrogen present in the structure of chitosan [31].

3.2. Effect of ionic strength on adsorption of MG

Effect of 0.07, 0.1, 0.3, 0.7 and 2 M NaCl solutions on adsorption of MG on silica gel was studied. Fig. 3(a)–(e) show adsorption isotherms of MG on silica gel from NaCl solutions at 308–328 K. As seen in Table 1, in the used concentration range of NaCl, q_{mon} values are less than its values in water. At each temperature, the q_{mon} values sharply decrease in low concentrations of NaCl (up to 0.3 M) and then increase in its higher concentrations, Table 1 and Fig. 4. In

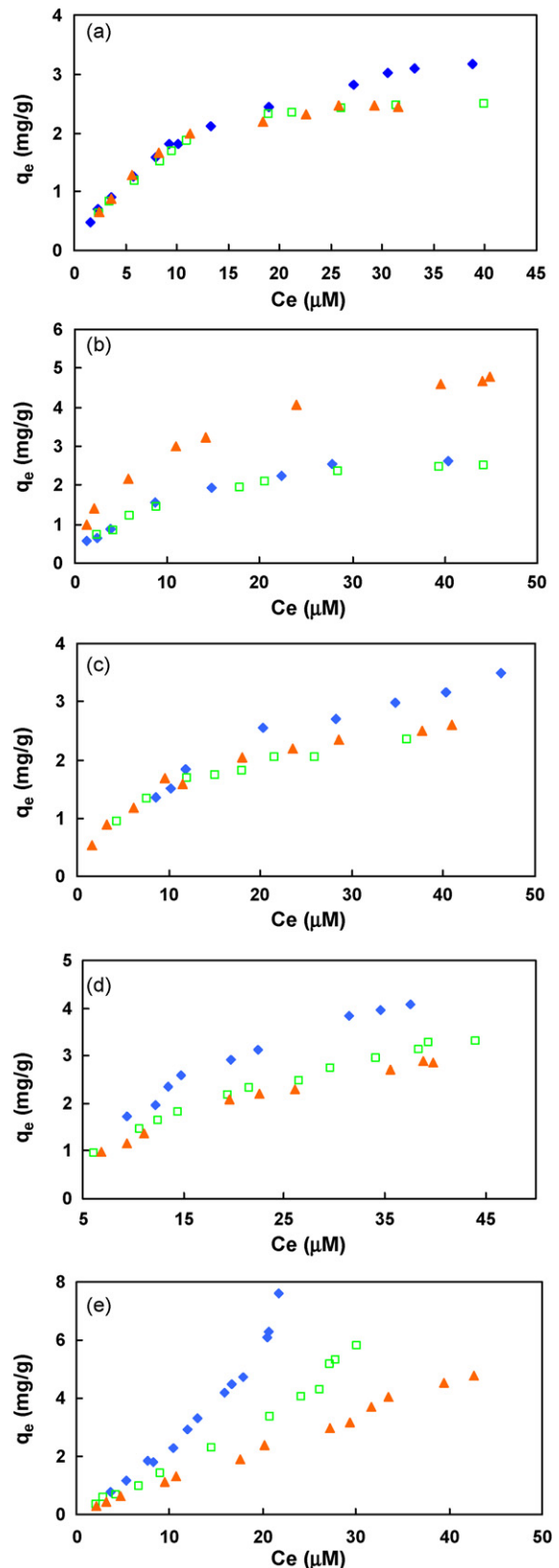


Fig. 3. Variation of q_e vs. c_e for adsorption of MG on silica gel in (a) 0.07, (b) 0.1, (c) 0.3, (d) 0.7 and (e) 2 M NaCl at \blacklozenge 308, \square 318 and \blacktriangle 328 K.

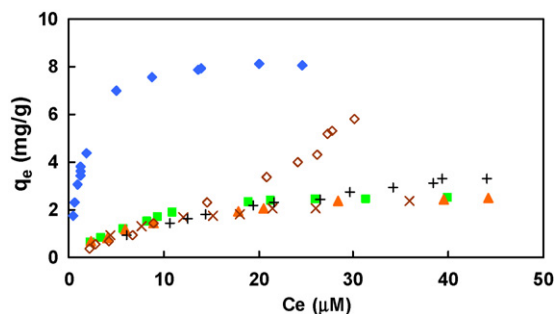


Fig. 4. Variation of q_e vs. c_e for adsorption of MG on silica gel in \blacklozenge water, \blacksquare 0.07, \blacktriangle 0.1, \times 0.3, $+$ 0.7 and \diamond 2 M NaCl at 318 K.

the former case, solubility at low ionic strength increases with salt concentration (salting in). Pairing of salt ions with charged groups of molecules shields intermolecular repulsion. In the latter case, solubility at high ionic strength decreases with salt concentration. Thus, solvent activity toward solubilization of hydrophobic solutes is reduced and NaCl salts out MG molecules and increases MG adsorption. Khataibe et al. reported the adsorption of cytochrome C (a basic protein) on the cermet and track-etched membranes and silica gel considerably reduced by adding sodium chloride to the solution [32]. As previously recorded, with increase in NaCl concentration up to 0.2 M, adsorption of MG on anaerobic granular sludge highly decreases [33].

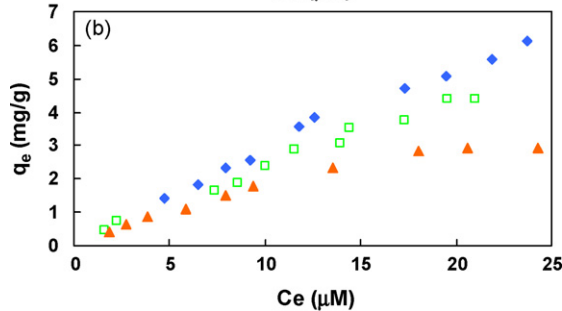
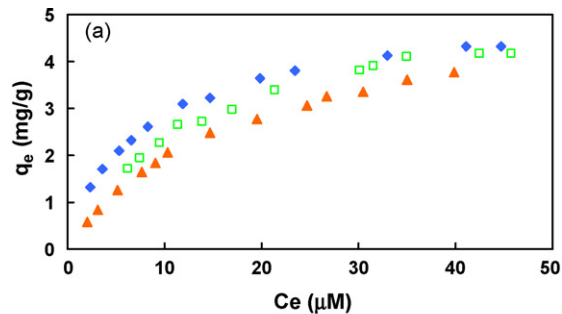


Fig. 5. Variation of q_e vs. c_e for adsorption of MG on silica gel from (a) 6.3×10^{-4} and (b) 5×10^{-3} M HCl at \blacklozenge 308, \square 318 and \blacktriangle 328 K.

Table 3
Parameters obtained from the Temkin, Langmuir and Dubinin–Radushkevich isotherms for the second region adsorption of MG on silica gel in different pH values at 308–328 K.

T (K)	Temkin			Langmuir			Dubinin–Radushkevich		
	c_1	c_2	R^2	K	q_{mon}	R^2	$\ln q_D$	E	R^2
pH 3.2									
308	1.097	1350209	0.997	170313	4.6	0.993	3.469	13.3	0.989
318	1.354	562850	0.995	70635	5.6	0.995	3.720	12.7	0.988
328	1.267	215727	0.997	60443	10.2	0.998	3.648	12.9	0.993
pH 2.3									
308	3.043	286613	0.978	7802	39.7	0.995	6.267	9.1	0.993
318	1.518	619883	0.889	29346	10.6	0.993	5.651	9.9	0.990
328	1.078	627640	0.955	38945	6.5	0.998	5.028	10.5	0.997

Dimension of c_1 , q_{mon} and q_D is in mg g^{-1} . Dimensions of c_2 , K and E are in M^{-1} , M^{-1} and kJ mol^{-1} , respectively.

Table 4
Parameters obtained from the Temkin, Langmuir and Dubinin–Radushkevich isotherms for the second region of adsorption of MG on silica gel in different weight percentages of 2-propanol-water binary mixtures at 308–328 K.

W _{2-PrOH} %	Temkin			Langmuir			Dubinin–Radushkevich		
	c_1	c_2	R^2	K	q_{mon}	R^2	$\ln q_D$	E	R^2
T= 308 K									
0.0%	1.866	7354517	0.990	774194	8.3	0.994	4.598	13.5	0.988
2.5%	1.642	2656933	0.992	318681	6.9	0.998	4.285	12.7	0.986
5.0%	1.223	3349730	0.994	305903	5.8	0.998	4.767	11.8	0.989
7.5%	1.127	2715677	0.995	308036	4.8	0.999	4.201	12.4	0.991
10.0%	0.934	2271553	0.999	267306	4.0	0.997	3.918	12.5	0.989
T= 318 K									
0.0%	1.817	5952605	0.982	596939	8.5	0.979	5.530	12.3	0.974
2.5%	1.664	2404304	0.994	282353	6.9	0.993	4.455	13.0	0.988
5.0%	1.386	2456592	0.980	277870	6.0	0.989	4.426	12.7	0.977
7.5%	1.063	3080025	0.992	326700	4.5	0.994	4.215	12.8	0.990
10.0%	0.926	2759206	0.975	308161	4.0	0.994	4.417	12.2	0.995
T= 328 K									
0.0%	2.005	4543359	0.984	437500	9.5	0.992	4.874	13.6	0.992
2.5%	1.761	2226914	0.981	261811	7.5	0.995	4.441	13.5	0.972
5.0%	1.534	2420165	0.994	272401	6.6	0.996	4.218	13.7	0.982
7.5%	1.173	3291396	0.983	373832	5.0	0.996	4.254	13.4	0.980
10.0%	0.936	3448393	0.987	386023	4.3	0.995	4.130	13.2	0.976

Dimension of c_1 , q_{mon} and q_D is in mg g^{-1} . Dimensions of c_2 , K and E are in M^{-1} , M^{-1} and kJ mol^{-1} , respectively.

The mean adsorption energy value, obtained from the Dubinin–Radushkevich equation, in different concentrations of NaCl at 308–328 K varies in the range of 9.0–14.2 kJ mol⁻¹, Table 2. As seen in Table 2, in the presence of NaCl interaction is endothermic and its ΔS value is positive. With increase in concentration of NaCl, ΔH and ΔS values of adsorption, up to 0.3 M, become more positive. But ΔH and ΔS values of adsorption decrease in 0.7 and 2 M NaCl solutions. The positive ΔH and ΔS values may be due to endothermic water structure breaking effect of salt [34] and desolvation of MG molecules in the presence of salt.

3.3. Effect of pH on adsorption of MG

Fig. 5(a) and (b) shows the adsorption isotherms of MG on silica gel from 5×10^{-3} and 6.3×10^{-4} M HCl solutions at 308–328 K which correspond to pH values of 2.3 and 3.2, respectively. As seen in Fig. 2, 5(a) and 5(b), in the used concentration range of HCl, adsorption capacities of MG are less than those values in water. In comparison to water medium, adsorption of MG was found to decrease as the surface charge became progressively more positive with decreasing pH values, Fig. 4. Thus, adsorption of MG is pH-dependent. It seems that at lower pH, the presence of H⁺ ions will compete with MG molecules for adsorption sites of silica gel, as reported for adsorption of methylene blue on zeolite [35]. This is due to the pH of the point of zero charge (pzc) of silica gel is approximately 2.9 [36]. When the pH is raised above this value, dissociation reaction of silanol (SiOH) groups ($pK_a = 6.8$) start to become important [37]. According to Iler the concentration of negative charges at the silica surface remains low up to about pH 6, before it increases up to a pH of about 10.7 [38]. Otherwise, with increasing HCl concentration probably due to increase in ionic strength of solution, q_{mon} value increases and ΔH value of adsorption becomes positive and ΔS value becomes more negative, Table 2. The mean adsorption energy value, obtained from the Dubinin–Radushkevich equation in acidic solutions at 308–328 K varies in the range of 9.1–13.3 kJ mol⁻¹, Table 3. It is necessary to say that experiments were not carried out under alkaline conditions, due to alkaline fading of MG [39,40], and in pH values less than 1.8, due to formation of MGH⁺² species [41,42].

3.4. Effect of 2-propanol on adsorption of MG

Effect of different weight percentages of binary mixtures of 2-propanol with water up to 10% on adsorption of MG on silica gel was studied at 308–328 K, Fig. 6(a)–(d). As seen in Table 4, in the used concentration range of 2-propanol, q_{mon} values are less than those values in water. As previously studied, adsorption of sudan I, acid orange 7, acid red 27, acid red 112 on fibrous activated carbon in water-ethanol mixtures decreased with increase in their ethanol weight percentage (up to 50%) [19].

As shown in Table 4, the mean adsorption energy (E) value, obtained from the Dubinin–Radushkevich equation at various weight percentages of 2-propanol at 308–328 K varies in the range of 11.8–13.7 kJ mol⁻¹, respectively.

As given in Tables 4 and 5, with increasing weight percentages of 2-propanol in binary solutions, q_{mon} values decrease and ΔH and ΔS values of adsorption in region 2 become more positive. In this region, adsorption occurs through chemical interaction between MG molecules and silica gel surface. In region 3, hydrophobic interaction between aromatic rings of MG molecules and adsorbed MG molecules has a central role and results in surface aggregates formation and data satisfy Eq. (4). In this region, MG molecules do not form bilayer on the surface and it seems that MG molecules bind to the surface through their =N⁺(CH₃)₂ group. In region 3, in each temperature with increase in weight percentages of 2-propanol, up to 7.5%, q_{mon} values increase and ΔH and ΔS values become more

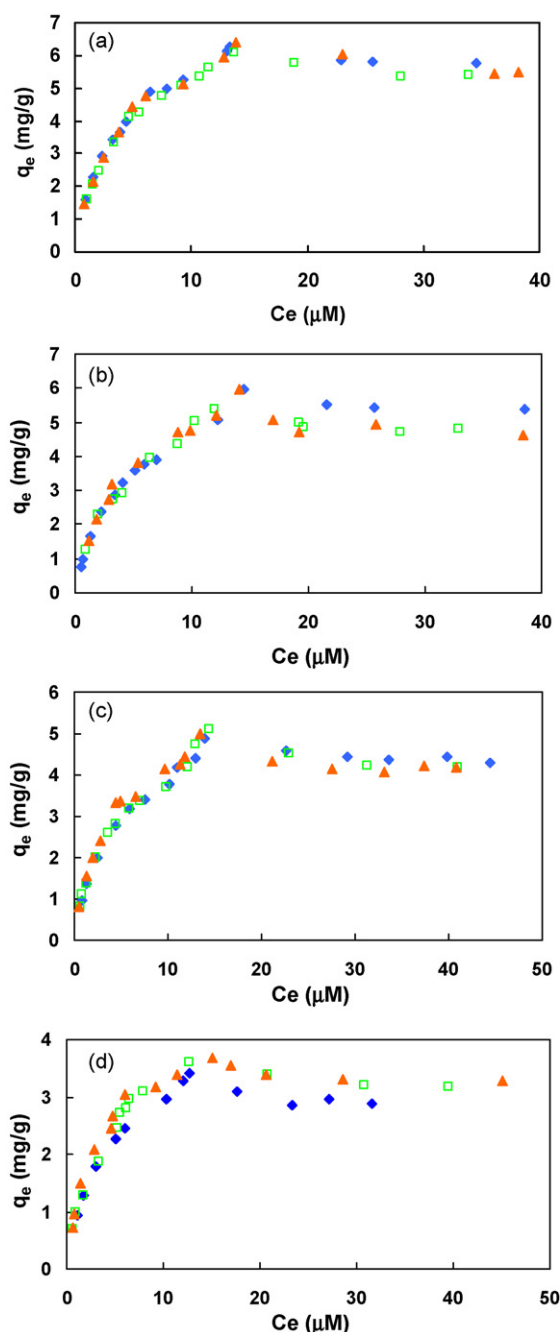


Fig. 6. Variation of q_e vs. C_e for adsorption of MG on silica gel from (a) 2.5, (b) 5, (c) 7.5 and (d) 10 weight percentage of 2-propanol in water at \blacklozenge 308, \square 318 and \blacktriangle 328 K.

Table 5

ΔH and ΔS values of second and third regions of adsorption of MG on silica gel from water and in different weight percentages of 2-propanol-water binary mixtures at 308–328 K.

$W_{2-PrOH}\%$	2nd region		3rd region	
	ΔH	ΔS	ΔH	ΔS
2.5%	-8.3	78.4	-10.2	62.5
5%	-4.9	89.0	-97.9	-221.8
7.5%	8.1	131.3	-117.2	-291.5
10%	15.4	153.7	82.4	358.9

ΔH and ΔS values are in kJ mol⁻¹ and J mol⁻¹ K⁻¹, respectively.

Table 6
Parameters obtained for third and fourth regions of adsorption of MG on silica gel in different weight percentages of 2-propanol-water binary mixtures at 308–328 K.

W _{2-PrOH} %	T (K)	3rd region			4A region			
		q _{mon}	K _{sa}	R ²	srd	q _{srd}	k _{rd}	R ²
2.5%	308	10.8	101313	0.998	1.34E-5	6.2	6049.0	0.991
	318	11.2	85577	0.981	1.38E-5	6.1	8806.3	0.999
	328	12.1	79519	0.981	1.38E-5	6.4	7607.8	0.996
5.0%	308	10.0	91651	0.962	1.44E-5	6.0	8776.5	0.962
	318	16.0	43172	0.964	1.20E-5	5.4	8213.4	0.996
	328	54.1	8810	0.977	1.41E-5	5.9	45104.0	0.977
7.5%	308	15.0	33858	0.931	1.39E-5	4.9	6310.7	0.997
	318	23.1	19330	0.995	1.45E-5	5.1	11385.6	0.980
	328	188.7	2038	0.992	1.34E-5	5.0	13526.0	0.950
10.0%	308	9.1	47210	0.990	1.27E-5	3.4	16563.4	0.998
	318	4.7	251469	0.916	1.27E-5	3.6	6212.2	0.998
	328	4.4	331387	0.995	1.50E-5	3.7	13985.6	0.994

Dimension of q_{mon} and q_{srd} is in mg g⁻¹. Dimensions of K_{sa}, k_{rd} and srd are in M⁻¹, M⁻¹ and M, respectively. Region 4B is as plateau. In region 4A, srd = c_{max} and q_{srd} = q_{max}.

negative and in 10% 2-propanol solutions become positive, Table 5. As seen in Tables 4 and 6, in each certain temperature and weight percentage of 2-propanol, K_{sa} values are less than K values of related region 2. This is due to steric hindrance of adsorbed MG molecules in region 2 and competition between aggregation of MG molecules in solution and their surface aggregation. With increase in weight percentages of 2-propanol, in each certain temperature, q_{srd} values and thus steric hindrance of adsorbed MG molecules decrease which finally results in increasing K_{sa} in 10% 2-propanol solution. In region 4A, Gibbs free energy of aggregation of MG molecules in solution, ΔG_a, is more negative than that of surface aggregation, ΔG_{sa}, [30] and this results in the reverse desorption of MG molecules and in region 4B, ΔG_a = ΔG_{sa} and this region is as plateau, Table 6.

4. Conclusion

Adsorption isotherms of MG on silica gel in the presence of NaCl, 2-propanol and acidic pH values were analyzed by ARIAN model. It was seen that adsorption capacity of surface decreases in low concentrations of NaCl and HCl (salting in) while its value increases with increase in their concentration (salting out). Binding constants of these processes were obtained using the Langmuir isotherms and adsorption process in water is exothermic and in the presence of NaCl is endothermic.

Adsorption of MG on silica gel decreases with increase in weight percentage of 2-propanol in its binary mixtures with water. In these series of isotherms, in low concentrations of MG, adsorption obeys the Langmuir isotherm (region 2). With increase in MG concentration, its surface aggregates form (region 3) and then reverse desorption of MG molecules occurs (region 4). Data of region 3 and 4 were analyzed by the bilayer and reverse desorption isotherms, respectively. Results show that binding constants of region 2 are bigger than those of region 3. The mean adsorption energy values showed that adsorption process occurs through chemical interaction.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2010.08.101.

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