

점토에 대한 2개 염기성 염료 RB5와 GB4의 경쟁 흡착

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Competitive Adsorption of Two Basic Dyes RB5 and GB4 on a Local Clay

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요약. 알제리에서 출토되는 소듐-교환된 Maghnia 점토에 대한 2개 염기성 염료인 RB5와 BG4의 흡착평형을 조사한 결과, 최대 흡착능은 각기 465.13 와 469.90 mg/g 으로 나타났다. ADMI 방법을 사용한 BR5 and BG4의 동시 흡착 실험에서 3개 다른 초기 농도비 R ($R = C_{(BR5)}/C_{(BG4)}$) 2.5/1, 1/1, 1/2.5 을 사용하였다. 염료 혼합물로부터 등온흡착 여부를 조사하여 경쟁 흡착인지를 알 수 있다. 점토 표면 위 흡착 활성자리를 위한 BR5 and BG4 간 매우 강한 상호작용 ($R = 1/1$)이 관찰되었다. RB 5 와 BG 4의 흡착 능의 비율 R' ($R' = Q_{e(mixture)}/Q_{e(single)}$)은 초기 농도 비율 R ($R = C_{(BR5)}/C_{(BG4)}$) 이 2.5/1, 1/1 and 1/2.5 인 경우에 대해 각기 0.86, 0.74 and 0.84 로 얻어졌다. Langmuir 와 Freundlich 모델이 각기 염료 뿐만 아니라 염료 혼합물의 흡착 거동에 잘 들어 맞음을 알 수 있었다.

주제어: 소듐-교환 점토; 흡착; 반응속도론; 등온; BR5 and BG4 염료, 경쟁

ABSTRACT. The equilibrium of adsorption of basics dyes RB 5 and BG 4 from a single dyes in the mixtures on the sodium-exchanged clay of the Maghnia (Algeria) was studied. The maximum adsorption capacities of BR5 and BG4 in single dyes were 465.13 and 469.90 mg/g respectively. In the simultaneous adsorption of BR5 and BG4 from mixture solutions, three different initials concentrations ratios R ($R = C_{(BR5)}/C_{(BG4)}$) were tested: 2.5/1, 1/1 and 1/2.5 using ADMI method. The isotherms adsorptions of dyes from the mixtures are characteristics of competition phenomenon. A very strong interaction between BR5 and BG4 for the active sites of adsorption of surface of clay is obtained for $R = 1/1$. The ratio R' ($R' = Q_{e(mixture)}/Q_{e(single)}$) of the adsorption capacity of BR5 and BG4 in the mixture were reduced by factor of 0.86, 0.74 and 0.84 for the initials concentrations ratios R ($R = C_{(BR5)}/C_{(BG4)}$) of 2.5/1, 1/1 and 1/2.5 respectively. The variation of the ratio of the adsorption capacity R' of BR5 and BG4 in the mixture solutions with initial concentration ratios R indicates that BR5 dye is slightly favourable in the competition adsorption than BG4. Langmuir and Freundlich models fit very well with adsorption behaviour of single dyes as well as the dyes in mixture solutions.

Keywords: Sodium-exchanged clay, Adsorption, Kinetics, Isotherm, BR5 and BG4 dyes, Competition

INTRODUCTION

The conscience of the potential impact of the colored effluents and more particularly the azo and triphenylmethanes dyes do not cease growing. Indeed, it is estimated that 10% of the annual production in dyes (approximately 7. 10⁵ tons) are evacuated during the various stages of application and clothes industry.¹ These effluents are important sources of pollution of water. The conventional methods of treatment of the aqueous

solutions containing dye (the oxydo-reduction and the exchanging resins of ions,² coagulation/flocculation,³ membrane separation,⁴ adsorption,⁵ the biological methods,⁶ and more recently the advanced processes of oxidation,⁷ do not allow obtaining threshold of pollution lower or equal to the maximum permissible concentration (MPC) imposed by the environmental recommendations. The adsorption appeared a very effective method for the reduction of the color in aqueous mediums. The clay of Maghnia (Algeria) introduces an alternate candidate,

potentially which may undergo beneficiation in the treatment of waste water. Several studies on the effectiveness of adsorbent materials were focused on the adsorption of mono-adsorbate system, however the waste water of textile industry contains several dyes (bi- or multi-adsorbate systems). Indeed the study of adsorption in the systems multi- adsorbed is very complex that is due to the independent factors including:

- (I) Possibility of the mutual interactions adsorbate-adsorbate;
- (II) Modification of the charge of surface of the adsorbent;
- (III) Competitive adsorption of dyes for the active sites on the surface of the adsorbent.

In this work, we presented the whole of the experimental results, namely the treatment of purification and the adsorption of RB5 and BG4 in the mono- and Bi-adsorbate systems by using ADMI method. The problem approached in this work is extremely important in the context of sustainable development which prevails today.

MATERIALS AND METHODS

Natural clay from Maghnia (Algeria) was used in a purified form. The basic dyes are provided by Acros Organics (99%). Basic red RB5 (C.I. 50040; chemical structure $C_{15}H_{17}ClN_4$; PM = 288.8 g/mole; $\lambda_{max} = 520 \text{ Nm}$ and $\epsilon = 25000 \text{ cm}^{-1} \text{ mole}^{-1} \text{ dm}^3$) and basic green BG4 (C.I. 42000; chemical structure $C_{23}H_{25}N_2.1/2C_2H_2O_4.C_2HO_4$; PM = 507.51 g/mole; $\lambda_{max} = 620 \text{ Nm}$ and $\epsilon = 147620 \text{ cm}^{-1} \text{ mole}^{-1} \text{ dm}^3$). The structure of basic dye Neutral red 5 (BR5) and Malachite green oxalates 4 (BG4) are displayed in Fig. 1.

Natural clay was purified from quartz and others no clay minerals by sedimentation following pre-treatment with 0.05 mol/L HCl to remove carbonates and sulphates, H_2O_2 solution

in the ratio of 1:30 (clay suspension: $H_2O_2 = v/v$) at 70°C to destroy organic matter. The $< 2 \mu\text{m}$ clay particle size fraction was saturated three times in Na^+ ions with 0.1 mol/L NaCl solution, and washed with distilled water to remove the excess of Cl^- ions, then separated by centrifugation, freeze dried at 60°C for 24 h and is crushed. The material resulting from different treatments will be indicated by clay-Na. The cation capacity of exchange CEC and total specific surface TSS of our clay-Na sample were estimated by the methylene blue method.⁸ The values of the CEC and TSS obtained are of 101.7214 meq/100 g of clay-Na and 673.9351 m^2/g respectively.

Aqueous dye solution stock was prepared by dissolving accurately weighed neat dye in distilled water to the concentration of 1 g/L.

Experimental solutions were obtained by successive dilutions.

The adsorption isotherms of single dye were carried out, in batch system at room temperature ($19 - 22^\circ \text{C}$), by using a known amount of clay-Na sample with solid/liquid ratio of 0.1 g/L. The initial BR5 or BG4 concentration solutions ranged from 5 to 60 mg/L. The pH of the dye solutions was adjusted by solutions of NaOH/ HCl (1 M) and stirred vigorously for 60 mn. At the end of the equilibrium period the solutions were filtered to separate the clay-Na and the residual concentration of BR5 or BG4 in the filtrate measured by UV/Visible spectrophotometer (Safa mc^2) at wavelength of 520 nm and 620 nm for BR5 and BG4 respectively. Linear calibrations curves were used in the determination of equilibrium BR5 and BG4 concentrations. The curves were based on standards in the concentration range from 5 to 30 mg/L.

The adsorption isotherms of the mixture of BR5 and BG4 dyes onto clay-Na were studied using the ADMI method. In our experiment, three initials concentrations ratios R ($R = C_{(BR5)}/C_{(BG4)}$) were tested: 2. 5/1, 1/1 and 1/ 2. 5. The procedures are similar to those in singles dyes. The amount of adsorption at equilibrium $Q_e(\text{mg/g})$ was calculated based on the following equation:

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

Where C_0 and C_e are the initial and equilibrium solution concentrations (mg/L) respectively. V is volume of the solutions (l), and m is the weight of Clay-Na (g) used.

The phenomena of adsorption are mainly defined by the models of Langmuir and of Freundlich. The linearized equation is given as follows.⁹

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max}K_1} + \frac{C_e}{Q_{max}} \quad (2)$$

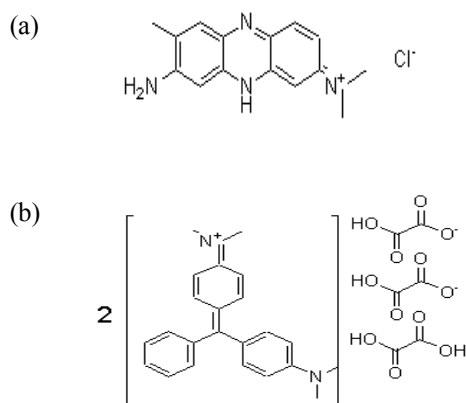


Fig. 1. The structures of basic dyes: (a) Neutral red 5 (BR5); (b) Malachite green oxalates 4 (BG4).

where C_e is the equilibrium concentration of adsorbate in the solution (mg/l), Q_e is the amount of adsorbate adsorbed at equilibrium per unit weight of clay-Na (mg/g), Q_{\max} is the maximum adsorption capacity (mg/g) and K_f is the adsorption equilibrium constant related to the sorption energy between the adsorbate and adsorbent (l/g). Q_{\max} and K_f are computed from the slopes and intercepts of the straight lines of the plot of (C_e/q_e) vs. C_e .

The logarithmic form of Freundlich equation is stated as follows.¹⁰

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \quad (3)$$

where K_f is roughly an indicator of the adsorption capacity (l/g) and $(1/n)$ is the adsorption intensity. A plot of $\log(Q_e)$ vs. $\log(C_e)$ leads to a straight with the slope of $(1/n)$ and an intercepts of $\log K_f$.

The adsorption isotherms of mixtures of the two basic dyes onto the clay-Na at room temperature were studied by the removal of ADMI¹¹ from aqueous solutions. This method is based on two principal criteria:

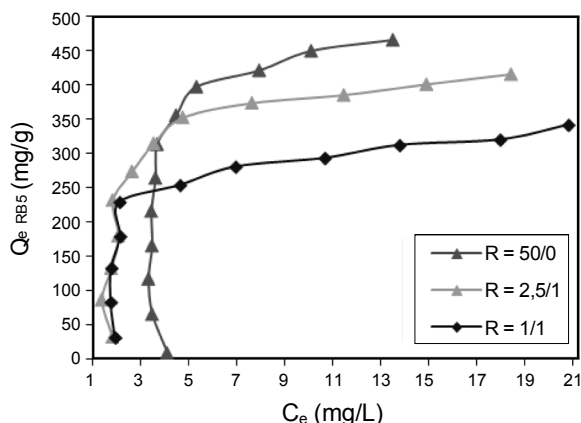


Fig. 2. Competitive equilibrium adsorption isotherms of BR5 dye in mono- and bi-adsorbed system with initial concentration ratios on clay-Na for $C_0 = 5 - 60$ mg/L, $m/v = 0.1$ g/L, $\text{pH} = 7$, $T = 19 - 22$ °C and contact time of 60 mn.

Table 1. Langmuir and Freundlich parameters of BR5 and VB4 dyes in mono- and bi-adsorbed system with initial concentration ratios on clay-Na for $C_0 = 5 - 60$ mg/L, $m/v = 0.1$ g/L, $\text{pH} = 5$, $T = 19 - 22$ °C and contact time of 60 min.

System	Experimental results			Langmuir model		Freundlich model		
$R = C_{(\text{BR5})}/C_{(\text{BG4})}$	$R^2 = Q_{e(\text{mixture})}/Q_{e(\text{single})}$	Q_{\max} (mg/g)	Q_{\max} (mg/g)	K_L (L/g)	R^2	K_f (L/g)	$1/n$	R^2
50 / 0	1.00	465.1316	588.2353	0.3208	0.9459	262.0669	0.2272	0.9338
2.5 / 1	0.86	401.0266	476.1905	0.5250	0.9688	222.9617	0.2296	0.8909
1 / 1	0.75	345.0777	333.3333	1.2500	0.9513	165.7366	0.2561	0.9880
1 / 2.5	0.84	386.3068	588.2353	0.2982	0.9796	151.8966	0.5182	0.9689
0 / 50	1.00	459.9068	555.5556	0.2432	0.8577	78.2102	0.8887	0.9929

- There are no mutual interactions between the two dyes;
- The total absorbance for a mixture dye solutions is equal to the summation of the absorbance of each dye;

$$A_\lambda = A_{\text{RB5}} + A_{\text{BG4}} \quad (4)$$

The adsorption capacities of each dye in mixture solutions are computed using the following equations:

$$A_{(\lambda_1)} = a_{\text{RB5}}C_{\text{RB5}} + a_{\text{BG4}}C_{\text{BG4}} \quad (5)$$

$$A_{(\lambda_2)} = a'_{\text{RB5}}C_{\text{RB5}} + a'_{\text{BG4}}C_{\text{BG4}} \quad (6)$$

where A_λ , A_{λ_1} , and A_{λ_2} are the absorbance of UV/VIS spectrometer at wavelength λ , λ_1 , and λ_2 , respectively; A_{BR5} and A_{BG4} are the absorbances of BR5 and BG4 at wavelength λ , respectively; a_{BR5} and a'_{BR5} are the absorbance coefficient of pure BR5 at wavelength λ_1 and λ_2 , respectively; a_{BG4} and a'_{BG4} are the absorbance coefficients of pure BG4 at wavelength λ_1 and λ_2 , respectively; C_{BR5} and C_{BG4} are the concentrations of BR5 and BG4 in the mixture solutions.

In order to obtain the adsorption capacity for each dye in mixture solutions, the concentrations C_{BR5} and C_{BG4} are calculated from equations (5) and (6).

RESULTS AND DISCUSSION

Figures 2 and 3 display the results of the adsorption isotherms of singles dyes and dyes in the mixtures with different initial concentration ratios R . The maximum adsorption capacities of BR5 and BG4 in single dyes were 465.1316 and 469.9068 mg/g respectively. However, in the competition adsorption of RB5 and BG4 from the mixture solutions, the adsorption capacity of each dye in the mixtures was decreased to 401.0266 mg/g of RB5 and 386.3068 mg/g of VB4 for $R = 2.5/1$ and $1/2.5$ respectively. A strong competition adsorption between BR5 and BG4 dyes for the active sites of clay-Na surface was observed for $R = 1/1$. These observations join those of former work of Pelekani and al.¹² for competitive adsorption between

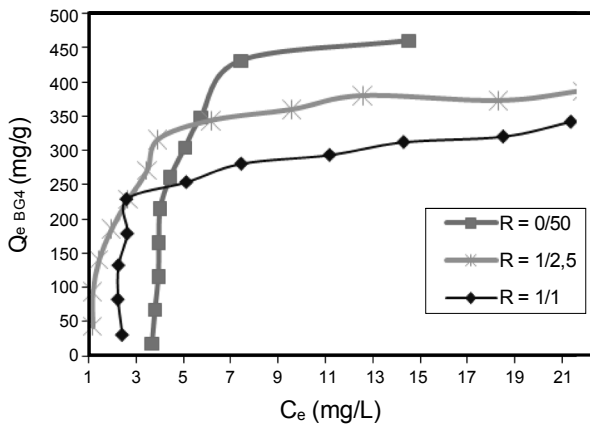


Fig. 3. Competitive equilibrium adsorption isotherms of BG4 dye in mono- and bi- adsorbed system with initial concentration ratios on clay-Na for $C_0 = 5 - 60$ mg/L, $m/v = 0.1$ g/L, $pH = 7$, $T = 19 - 22$ °C and contact time of 60 mn.

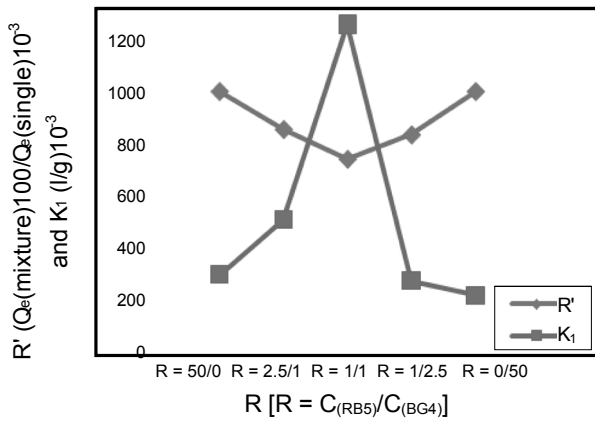


Fig. 4. Variation of R' and K_1 parameters as function of R during the competitive equilibrium adsorption isotherm of VB4 and BR5 dyes in mono- and bi- adsorbed system with initial concentration ratios on clay-Na.

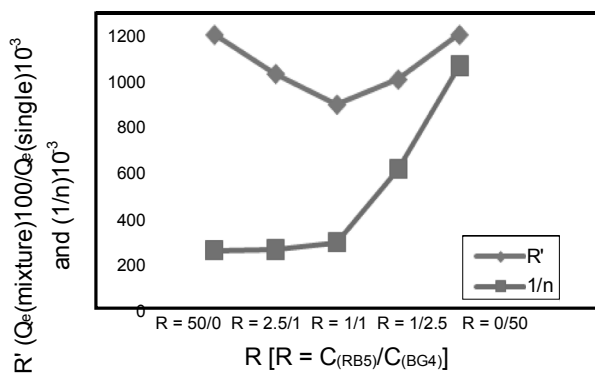


Fig. 5. Variation of R' and $1/n$ parameters as function of R during the competitive equilibrium adsorption isotherm of VB4 and BR5 dyes in mono- and bi- adsorbed system with initial concentration ratios on clay-Na.

methylene blue and atrazine on the activated carbon.

Table 1 lists Langmuir and Freundlich linearized models applied for the obtained experimental results of the adsorption isotherms of singles dyes and dyes in the mixtures with different initial concentration ratios. Freundlich model was fitted to the adsorption data slightly better than the Langmuir model with highly significant coefficients of regression ($R^2 > 0.94$), which represents a heterogeneous surface for adsorption.

These results are similar to those obtained for the adsorption of the reactive dyes (RY84, RR147 and RB160) on the wool.¹³ To understand which dye is more favorable in the competitive adsorption, the experimental adsorption data were expressed in term of the capacity of maximum adsorption ratio R' ($R' = Q_e(\text{mixture})/Q_e(\text{single})$). For the adsorption in singles dyes, R' has a value of 1.00 for RB5 and BG4 respectively. However, in the mixtures of dyes, the values of the ratio R' are 0.86, 0.75 and 0.84 respectively for R equal to 2.5/1, 1/1 and 1/2.5. The order of competitive adsorption of clay with respect to RB5 and BG4 is the following:

$$R'_{(BG4 \text{ single})} = R'_{(RB5 \text{ single})} > R'_{(R=2.5/1)} > R'_{(R=1/1)} > R'_{(R=1/2.5)}$$

It indicates that the competitive adsorption seems to favor the dye RB5 slightly than BG4. This behavior of preferential adsorption can be explained in point of view of molecular weight of the dyes ($RB5 = 288.8$ g/mole and $VB4 = 507.51$ g/mole). The RB5 with one weaker molecular weight will compete with faster for the actives sites than VB4. The similar phenomena have been observed in adsorption of Dye AAVN and RB4 in of acid solutions on chemically cross-linked chitosan beads.¹⁴

The plot of experimental data R' and the theoretical data deduced from the adjustments of Langmuir K_1 and Freundlich $1/n$ vs. initial concentrations ratios R are illustrated on Figures 4 and 5. It was found that R' behaves inversely with K_1 for both dyes in the range of the R explored, whereas R' behaves opposite manner with $1/n$ for R ranged from 2.5/1 to 1/1, on the other hand, it seems that R' and $1/n$ show a similar behavior when R varying from 1/1 to 1/2.5.

CONCLUSION

This study investigated the equilibrium of the adsorption of two basic dyes on the clay-Na in mono- bi- adsorbate aqueous solutions systems. The clay-Na exhibits very high adsorption capacities to remove the basic dyes with maximum adsorption capacity of BR5 and BG4 in single dyes of 465.13 and 469.90 mg/g respectively. In the mixtures, the adsorption capacity of each dye was reduced by a factor of 0.86, 0.75 and 0.84 for $R = 2.5/1$, 1/1 and 1/2.5 respectively. A strong competition adsorp-

tion between BR5 and BG4 dyes for the active sites of clay-Na surface was observed for $R = 1/1$ and the competitive adsorption seems to favor the dye RB5 slightly than BG4.

Freundlich model was fitted to the adsorption data slightly better than the Langmuir model in single dyes as well as the dyes in mixture solutions.

The capacity of maximum adsorption ratio R' behaves inversely with K_1 for both dyes in the range of the R studied. However R' behaves opposite manner with $1/n$ for R ranged from 2.5/1 to 1/1, whereas, it seems that R' and $1/n$ show a similar behavior when R varying from 1/1 to 1 2,5.

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