ADSORPTION OF DISP YELLOW RGFL (DYR) DYE BY CETYLTRIMETHYLAMMONIUM BROMIDE (CTAB) – MODIFIED BENTONITE

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TÓM TẮT

NGHIÊN CỨU HẤP PHỤ THUỐC NHUỘM DISP VÀNG RGFL (DYR) **BẰNG BENTONIT BIẾN TÍNH CETYL TRIMETYL AMONI BROMUA (CTAB)**

Trong bài báo này, bentonit biến tính CTAB được sử dụng làm chất hấp phụ để nghiên cứu động học và đẳng nhiệt hấp phụ của DYR trong dung dịch nước ở các nồng độ thuốc nhuộm, nhiệt độ và pH khác nhau. Đường đẳng nhiệt dữ liệu thực nghiệm được phân tích theo hai phương trình Langmuir và Freundlich và mô hình Freundlich là phù hợp nhất với dữ liệu đẳng nhiệt và cân bằng. Dung lượng hấp phụ theo Lungmuir đối với thuốc nhuộm DYR là khoảng 340 mg/g. Khả năng loại bỏ màu tối đa quan sát được ở pH 1. Động học hấp phụ của DYR tuân theo mô hình độc học bậc 2.

Keywords: adsorption, DYR, CTAB, bentonite

1. INTRODUCTION

Organic dyes are familiar pollutants in wastewater, which could generate a great deal of toxic substances. Their source can be tracked down from food, paper-making, leather, paint, plastics, cosmetics and textile industries, resulting in high organic pollutant content, deep color, and serious impact on water quality inevitably [1, 2]. Among these colored compounds, there are many toxic compounds or even carcinogenic compounds. Water polluted by these compounds not only harms the environment, but also affects aquatic life. In addition, these compounds are stable to light, temperature and oxidants.

Several technologies have been developed for dye removal including adsorption, chemical and electrochemical oxidation, super filter film, membrane separation, and coagulation [3]. Amongst the treatment methods, adsorption has been found as the most effective method to remove colored compounds from polluted water. The advantage of this method is that the materials used for removal of colored compounds are abundant in nature, cheap and not toxic, therfore do not affect to enviroment. A number of studies used adsorbents derived from nature or cheap precursors such as zeolite, rice husk, coconut husk fiber and sawdust to treat polluted water, have reported. Outstanding of above materials, clays and clay minerals are widely used as adsorbents due to their high specific surface area [4, 5]. Bentonite, which is consisting essentially of montmorillonite group, is one of natural clays composed of two silica tetrahedral sheets with an octahedral alumina sheet, composed of two silica tetrahedral sheets with an octahedral alumina sheet. Bentonite surface is negatively charged due to isomorphous replacement of Al^{3+} for Si^{4+} in the tetrahedral layer and Mg^{2+} for Al^{3+} in the octahedral layer. This negative charge is balanced by exchangeable cations such as Na^{+} in the lattice structure. The layered structure of bentonite allows swelling after wetting. Na^{+} and Ca^{2+} are hydrates in the presence of water; therefore there is a hydrophilic environment at clay surface and natural bentonite is not an effective adsorbent for the nonpolar organic compounds in water. Surface properties of bentonite can be greatly changed by using surfactants or modifying agents. These modified bentonites have been widely used in wastewater treatment processes.

In this study, we report removal of Disp Yellow RGFL (DYR) dye from aqueous solution using modified bentonite as an organo-adsorbent.

2. EXPERIMENTAL

2.1. Chemicals

Cetyltrimethylammonium bromide (CTAB) with molecular formula of $C_{19}H_{42}NBr$ was purchased from Merck with the molecular mass of 364.46 $g.mol^{-1}$ and boiling point in the range from 250 to 256 ^{o}C.

Disp Yellow RGFL (DYR) with molecular fomula of $C_{18}H_{14}N_4O$, molecular mass of 302.33 g/mol and maximum absorption band of 445 nm, was used as an adsorbed compound.

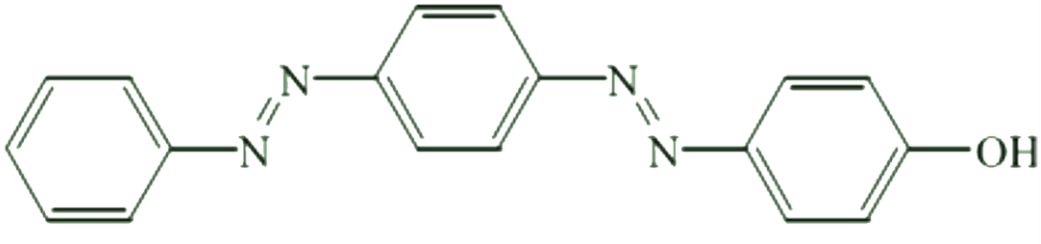

Figure 1: Structure formula of Disp Yellow RGFL.

2.2. Preparation of modified clay

Organo-adsorbent was obtained by modification of Binh Thuan bentonite. The modification process was carried out by dried method using NaCl and cetyltrimethylammonium bromide as follows: 2 g of Binh Thuan bentonite was dispersed in 250 mL saturated solution of NaCl with the help of magnetic stirrer for 2 hours. The mixture was then filtered and washed with a plenty of distilled water. In order to fully exchange between cations in bentonite and sodium ions, this procedure was repeated two times more. The obtained sodium-bentonite (Na-Bent) was again dispersed in a 250 mL-beaker contaning 100 mL of distilled water at 70 ^{o}C. To this mixture, add an amount of CTAB solution with the CTAB/Bent ratio of 130 mg/100 g. The obtained mixture was then adjusted to pH value of 9 and kept at 60 ^{o}C for 4 hours under stirring condition (500 rpm). The mixture was afterward filtered and washed with plenty of distilled water. The obtained solid clay was finally dried at 80 ^{o}C for 24 hours and ground into fine powders. The obtained clay powders have particle size varying in the range from 10 to 15 µm and contain of about 24.76 %wt of quaternary ammonium groups.

2.3. Adsorption study

A certain amount of modified bentonite was added to 50 mL aqueous solution of DYR with a given concentration at a certain pH and temperature. The mixture was then stirred for 4 hours under stirring condition with the speed of 150 rpm. Afterward, aqueous solution was separated from solid bentonite by contrifuging method. The remained concentration of DYR in aqueous solution after adsorption was finally determined by UV-Vis spectroscopy using UV-Vis spectrophotometer purchased from Thermo Scientific GENESYS. Effects of pH on the DYR removal of modified bentonite were carried out at different pH values ranging from 1 to 9. The efficiency of DYR removal was computed using the following equation:

$$\frac{C_i - C_o}{C_i} x100$$

Where C_i is the initial dye concentration and C_0 is the final dye concentration after adsorption.

The adsorption kinetics was investigated by analyzing the adsorptive removal of the dye from aqueous solution at different time intervals. For adsorption isotherms, DYR dye solution of different concentrations was agitated with a known amount of adsorbent till equilibrium was reached. The samples were collected at regular time intervals and the residual concentration of dye in the aqueous phase was analyzed after centrifuging.

3. RESULTS AND DISCUSSION

3.1. Effect of initial pH

Solution pH is recognized as an important parameter that dominates the adsorption process at solid-liquid interfaces, generally. The effect of initial pH on the

adsorption of DYR by CTAB-modified bentonite was studied by varying the pH of the dye solution from 1.0 to 9.0 for initial concentration of 100 mg dye/L, at 25 ^{o}C in 6 h.

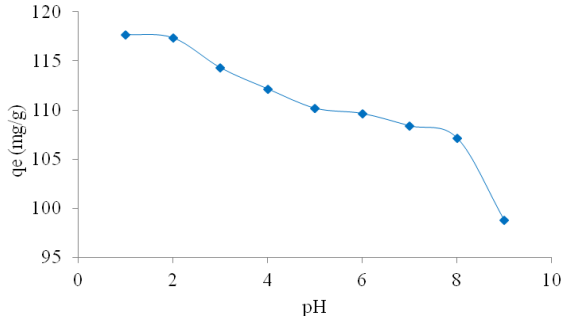

Figure 2: Effect of initial pH on DYR adsorption.

As can be seen in Figure 2, the adsorption capacity kept decreasing with the increasing of solution pH, adsorption capacity at equilibrium q_e decreases from 117.68 mg/g at pH 1 to 98.75 mg/g at pH 9. The fact that the adsorption capacity of DYR on CTAB-bentonite at pH 1 was higher than that at other pH values, was attributed to electrostatic attraction between the cationic dye and the negatively charged adsorbent.

The optimal pH value was selected at pH 1 for all the following experiments.

3.2. Effect of temperature

In general, adsorbability of adsorbent depends on the temperature of the solid-liquid interface. In order to investigate to effect of temperature on the DYR adsorption, rate of adsorption was studied in the temperature range from 25 to 60 ^{o}C. The obtained results are depicted on Figure 3.

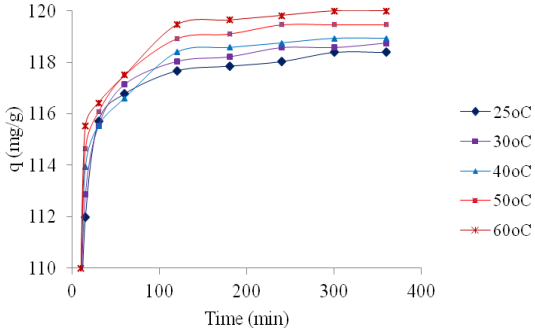

Figure 3: Effect of temperature on DYR adsorption.

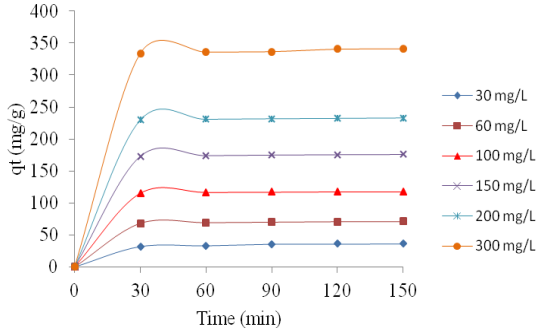

Figure 4: Effect of initial concentration and time on DYR adsorption.

As show in Figure 2, when temperature icreases from 25 to 60 ^{o}C, the adsorption capacity increases from 118.393 mg/g (at 25 ^{o}C) to 120 mg/g (at 60 ^{o}C). This means that the temperature has little effect on DYR adsorption on bentonite material, and the optimal temperature for DYR adsorption was selected at 25 ^{o}C.

3.3. Effect of initial concentration and time on DYR adsorption

Figure 4 represents the adsorption capacities obtained at the different initial DYR concentrations ranging from 30 mg/L to 300 mg/L, and adsorption time intervals. As show in Figure 4, DYR adsorption occurs with a high rate at the first 30 minutes, then

reaches equilibrium or near equilibrium state. As the increase of initial concentration of DYR, the adsorption capacity increases. The adsorption capacity is of 36.251 mg/g at the initial concentration of 30 mg/L and reaches the value of 341.067 mg/g at the initial concentration of 300 mg/L. This result shows that DYR adsorption of modified bentonite is affected significantly by initial concentration of DYR.

3.4. Adsorption isotherm study

Figure 5 and 6 show Freundlich and Langmuir models for DYR adsorption on CTAB-modified bentonite at different temperatures. All relative coefficients obtained from these isotherm models are listed in table 1.

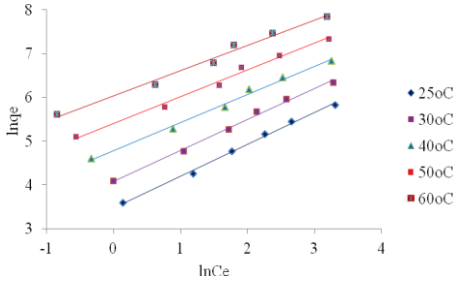

Figure 5: Freundlich isotherm model at different temperatures.

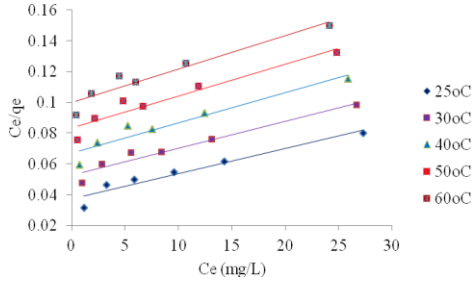

Figure 6: Langmuir isotherm model at different temperatures.

Table 1: Parameters obtained form isotherm models

T(°C)	Freundlich model			Langmuir model		
	R^2	K_f	N	R^2	q_m	b
25	0.996	32.073	1.372	0.935	333.333	0.081
30	0.994	35.981	1.418	0.946	333.333	0.094
40	0.989	43.207	1.543	0.911	333.333	0.111
50	0.989	49.452	1.631	0.918	500.000	0.087
60	0.985	56.656	1.739	0.920	500.000	0.105

As illustrated in Figure 6, the DYR adsorption on CTAB-bentonite is fitted better with Freundlich model. This result suggests that the DYR adsorption on bentonite belongs to physical adsorption with relative coefficients (R^2) of 0.996; 0.994; 0.989; 0.989 and 0.985 at 25, 30, 40, 50 and 60 °C, respectively.

3.5. Kinetic coefficients of DYR adsorption

Figure 7 and 8 show curves of $lg(q_e-q_t)$ and t/q_t versus time t, in which q_e and q_t are adsorption capacities at equilibrium and time t, respectively.

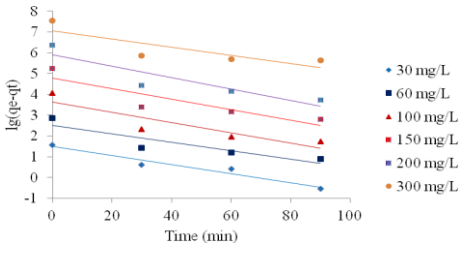

Figure 7: The 1st order kinetic model at different concentrations

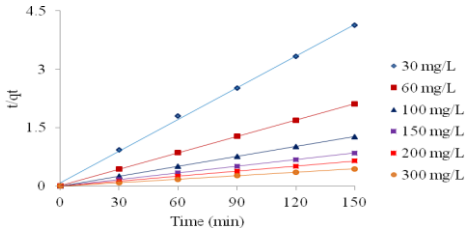

Figure 8: The 2nd order kinetic model at different concentrations

Values of rate constants of the first and second order kinetic equation of DYR adsorption, K_1 and K_2, adsorption capacity at equilibrium q_e, and relative coefficient, R^2 obtained from fitting experimental data are listed in Table 2.

Table 2: Kinetic coefficients of DYR adsorption

C (mg/L)	Pseudo-1st -order kinetic model			Pseudo-2nd - order kinetic model		
	q_e (mg/g)	K_1	R^2	q_e (mg/g)	K_2	R^2
30	30.409	0.048	0.943	37.037	0.010	0.998
60	31.915	0.046	0.823	71.429	0.016	0.999
100	42.462	0.055	0.804	125.000	0.021	0.999
150	61.944	0.058	0.808	200.000	0.013	0.999
200	78.704	0.062	0.819	250.000	0.016	0.999
300	114.815	0.044	0.699	333.330	0.004	0.999

As can be seen, values of the relative coefficients for the pseudo-second-order kinetic model are more similar than that of in the pseudo-first-order kinetic model. This suggested that, the DYR adsorption on CTAB-bentonite can be represented by the second order kinetic model.

4. CONCLUSION

The study proves that the synthesized organo-bentonite can remove DYR from aqueous solution with a relatively high efficiency. At pH value of 1, efficiency reaches value of 94.14 %. The adsorption reaches equilibrium state after 2 hours and obeys the pseudo-second-order kinetic model and Freundlich isotherm model.

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