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Removal of Textile Dye by Bentonite and Organo-Bentonite

RAMAZAN ALI DIANATI TILAKI
Department of Environmental Health, Faculty of Health, Mazandaran University of Medical Sciences, Km 18 Khazar Abad Road, Sari, Iran
Fax: (98)(151)3542473; Tel: (98)(151)3543085; E-mail: dianati.tilaki@gmail.com

In this study, bentonite was modified by alkyl dimethyl benzyl ammonium chloride (ADBAC) in order to obtain an alternative sorbent for dye removal from textile effluents. Two dyes using in textile industry were examined in this study. Aqueous solutions prepared from disperse blue 56 and pigment blue 60 were used and batch kinetic and isotherm experiments were carried out. Data were evaluated for applicability to the Langmuir and Freundlich isotherm models and the removal capacity of organo-bentonite was compared with that of ordinary bentonite. The adsorption was reached in equilibrium within 6 h of contact time. Adsorption kinetics obeys a Pseudo-second order reaction. Adsorption isotherms were fitted with Langmuir and Freundlich models. Corresponding constants of both models were calculated. Adsorption efficiencies were increased with increasing the sorbents dose. Results indicated that 85 and 78 % removal of disperse blue and pigment blue, respectively by organo-bentonite compared with a removal of 52 and 45 % achieved by ordinary bentonite. Adsorption capacity of bentonite for dye removal can be effectively increased by modification with commercial cationic detergent.

Key Words: Pigment blue, Disperse blue, Organo-bentonite and Adsorption.

INTRODUCTION

In the textile industries a great amount of dyes are used for colouring the products. There are many points that dyes and non biodegradable organics enter to the effluents. During the two last decades many researchers attempted to find eco-friendly technologies for removal of dyes from textile effluents[1]. Textile industries use different methods for dye removal in the treatment processes including floatation, chemical coagulation, chemical oxidation, biological treatment, electrolysis, photo catalysis and adsorption[2-6]. In the adsorption process, activated carbon is one of the most used sorbents for removal of organics including dyes from water environment[7,8]. But activated carbon is an expensive material. Many researchers focused their study to find alternative adsorbents that are cost-effective for industrial dye sorption. Different categories of materials were studied as alternative sorbents. Mineral materials such as natural clay, bentonite, vermiculite, illite, kaolinite and sepeolite have been used for industrial dye removal in the numerous studies[9-16].

Bentonite is one type of clay which is cheap and available in many countries. Bentonite is a 2:1 layered silicate, the inner layer is an octahedral sheet which is located between two tetrahedral sheets. There is Si^{4+} in tetrahedral and Al^{3+} in octahedral sheets, respectively. The substitutions of $A1^{3+}$ for Si^{4+} in the tetrahedral layer and Mg^{2+} or Zn^{2+} for $A1^{3+}$ in the octahedral layer results a negative charge on the surface of bentonite. The charge imbalance is offset by exchangeable cations such as Na^+ or Ca^{2+} on surfaces of layers[17]. Bentonite is hydrophilic and ineffective for adsorption of organic molecules. Since there are exchangeable cations on the surface of bentonite layers, hydrophobic cationic surfactants can be substituted by these cations. By substitution of Na^+ with cations of detergent, bentonite can be modified and absorb organic molecules by organophilic tail of detergent molecules[18]. Modification of bentonite is a method to increase adsorption capacity of cheap mineral sorbents for removal of organic pollutants from water environment. This method to convert organophobic minerals to organophilic sorbents for adsorption of different organics has been studied during last decade. Limited researchers studied on the adsorption of textile dyes by using organoclay[18-23]. It has however not been studied textile dye removal using organo-bentonite modified by alkyl dimethyl benzyl ammonium chloride (ADBAC).

The present study involves preparation of organically modified bentonite, batch experiments to delineate the kinetics of dye adsorption, comparison of the sorption capacity and effect of sorbent masses of bentonite and organo-bentonite to remove pigment blue 60 and disperse blue 56 from aqueous solutions.

EXPERIMENTAL

Bentonite used in this study was industrial grade produced in Semnan, Iran. Characteristics of the bentonite are given in Table-1. Cationic detergent to prepare organo-bentonite was alkyl dimethyl benzyl ammonium chlorides (ADBAC) commercial grade (benzalkonium chloride) produced in Iran. The dyes utilized were disperse blue and pigment blue with λ_{max} (wavelength at which maximum absorbance occurs) = 580 and 575 nm, respectively, was obtained from textile industry, Sari, Iran.

TABLE-1
ANALYSIS OF BENTONITE

Parameter	Weight (%)
SiO_2	68.259
Al_2O_3	11.436
Fe_2O_3	2.801
CaO	0.406
Na_2O	2.859
LiO	10.830
K_2O	0.487

Preliminary treatment of bentonite: A total of 100 g bentonite was washed with enough tap water and placed in Imhoff cones for sedimentation (for discarding impurities). The slurry of bentonite separated from cones was dried at 110 ºC in the oven. Dried bentonite was used as ordinary bentonite.

Preparation of Na-bentonite: Na-bentonite was prepared by contacting natural bentonite with 0.1 M NaCl solution for 24 h on a shaker. Then the suspension was filtered through a Buchner funnel and the filtration cake was rinsed twice with enough distilled water and dried at 105 ºC in the oven.

Preparation of organo-bentonite: A total of 50 g of preliminary treated bentonite powder was added to 500 mL of cationic detergent (ADBAC 40 % vol.). The mixture was agitated on a rotary shaker for 24 h at room temperature. The ADBAC-bentonite suspension was then washed with distilled water repeatedly. Rinsing was repeated until the filtrate was chloride free (tested with 0.1 M $AgNO_3$). The organo-bentonite was dried at room temperature and stored in bottles for experimental use.

Aqueous dye solutions were prepared by dissolving two dyes 1-pigment blue 60 (dye 1) and 2-disperse blue 56 (dye 2) in distilled water.

Effect of contact time: In this step initial concentration of each dye tested was 50 mg L^{-1}. Batch adsorption experiments were carried out by allowing an accurately weighed amount of natural bentonite (0.25 g) and organo-bentonite (0.1 g) separately to contact with dyes solutions of known concentration. These sorbents were added to two set of narrow-neck bottles (one set for pigment blue and another for disperse blue) each containing 50 mL dye solution. The bottles were shaken at room temperature for a given time: 10, 20, 40 min and 1, 2, 4, 6 and 18 h on a shaker (Rotomix, Behdad, Iran).

Effect of sorbent dose: Three doses of bentonite (1, 2 and 5 g L^{-1}) and 3 doses of organo-bentonite (0.5, 1.0 and 2.0 g L^{-1}) were added to dye solution (50 mL, 50 mg L^{-1}) separately. The bottles were shaken at room temperature for 6 h.

Sorption isotherm: In the sorption isotherm experiments, a predetermined weight of bentonite (0.25 g) and organo-bentonite (0.1 g) were added to bottles containing 50 mL of dye solutions with different concentrations (10, 20, 50 and 100 mg L^{-1}) separately and subsequently placed on a shaker for 6 h at 20 ºC. Isotherm experiments were carried out on an unaltered pH value of the dye solution (pH = 7.3). In all the experiment stages mentioned above, after contact time, the content of bottles were centrifuged for 0.5 h at 1200 g (Heraeus-Christ, Germany) and the supernatant was subsequently analyzed for residual concentration of dye by using a Jasco-7800 (Japan) UV/vis spectrophotometer. The amount of dyes sorbed was determined by difference between the initial and final concentrations.

RESULTS AND DISCUSSION

The amount of dye adsorbed onto bentonite and organo-bentonite as a function of contact time is shown in Fig. 1. The initial concentration of each dye in the solution was 50 mg L^{-1}. Equilibrium adsorptions were reached during 6 h since there is almost no further increase in the adsorption with time.

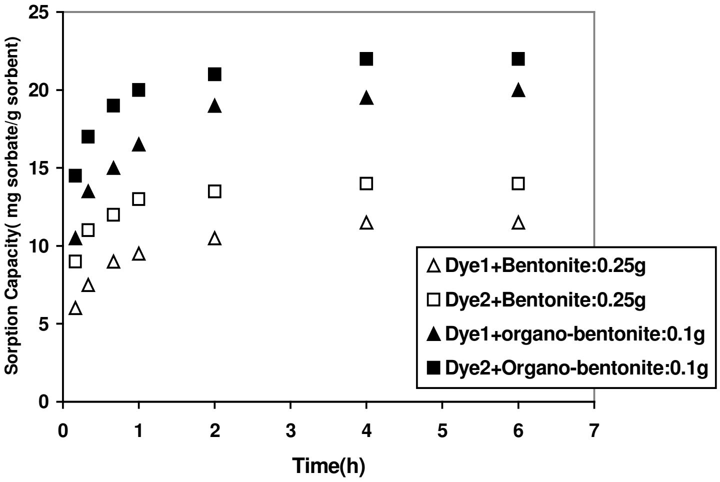

Fig. 1. Adsorption kinetic of two examined dye by bentonite and organo-bentonite

Voudrias *et al.*[16] reported that the contact time for the adsorption of reactive blue 21 onto bentonite to attaining equilibrium was 72 h. Jovic-Jovicic *et al.*[22] reported the time taken to reach equilibrium for adsorption of acid orange 10 onto HDTMA-bentonite was 2 h. According to the results presented in Fig. 1, the amount of dye adsorbed per unit weight of sorbent at equilibrium, q, were 20-22 for organo-bentonite and 11-14 for ordinary bentonite. Ceyhan and Bayas[24] reported that q (mg dye/g sorbent) for adsorption of blue 4BL on HDTMA-bentonite was in the range of 25-30.

Fig. 1 shows most of dye adsorption take place in the first ten minutes of contact and then sorption was more slowly until the equilibrium. This trends means there are strong attractive forces between the dye molecules and sorbents. The Lagergren first order rate equation is written as:

$$\log (q_e - q_t) = \log q_e - k_1t/2.303 \quad (1)$$

The pseudo-second order kinetic rate equation described by Ho and McKay[25] is expressed as:

$$t/q_t = 1/k_2q_e^2 + t/q_e \quad (2)$$

where k_1 and k_2 are the rate constant of first and pseudo second order adsorption (g mg^{-1} min^{-1}), respectively. q_t is sorption capacity in contact time of t and q_e is sorption capacity at equilibrium. A plot of log (q_e - q_t) *versus* t gives a straight line as can be seen in Fig. 2, confirming the applicability of first order rate expression. Both first and second order kinetics model were tested and values of q_e, k_1, k_2 and R^2 are presented in Table-2. Values of k_1 and k_2 were obtained from slope and intercept of straight lines (plots of 2 and 3).

Since the correlation coefficients for the pseudo second order kinetics model are closer to unity than the corresponding correlation coefficients for the first order kinetic model, the second order kinetics model was proven to be more adequate.

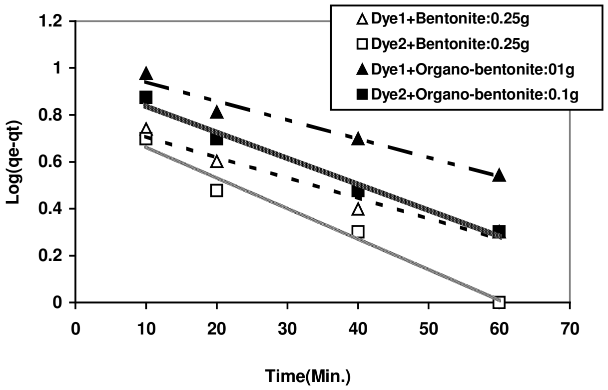

Fig. 2. Lagergren plots for the adsorption of dyes by sorbents at dye concentration of 50 mg L^{-1}

TABLE-2
KINETIC PARAMETERS OF DYES BY SORBENTS

Dye + sorbent	Pseudo second order			Pseudo first order	
	q_e	k_2	R^2	k_1	R^2
Dye1 + bentonite	11.5	0.0301	0.9987	0.0202	0.9611
Dye2 + bentonite	14.0	0.0354	0.9983	0.0303	0.9797
Dye1 + organo-bentonite	20.0	0.0076	0.9991	0.0186	0.9639
Dye2 + organo-bentonite	22.0	0.0083	0.9994	0.0257	0.9829

Jovic-Jovicic *et al.*[22] reported that adsorption of acid orange 10 onto HDTMA-bentonite obeys both the first-order and pseudo second-order kinetics model. Yeddou and Bensmaili[26] reported that adsorption of basic red 46 onto mixture of bentonite and wood-sawdust obeys with pseudo second order kinetic model. Khenifi *et al.*[21] reported correlation coefficients of supranol yellow 4GL sorption on CTAB-bentonite according to first and second order kinetics were 0.966 and 0.995, respectively and reported that similar trends were observed[20] for the adsorption of commercial basic blue dye (BB69) on activated clay (Fig. 3).

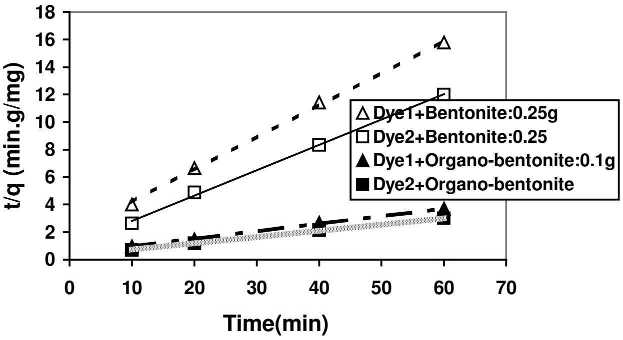

Fig. 3. Pseudo-second order kinetics for dye removal by sorbents

Classical adsorption models, Langmuir and Freundlich were used to describe the equilibrium between adsorbed dye on the mixture and dye in solution (C_e) at a constant temperature. The Langmuir equation which is valid for monolayer sorption onto surface of finite number of identical sites is given by eqn. 3.

$$C_e/q_e = 1/q_{max}\cdot k_L + C_e/q_{max} \quad (3)$$

where q_{max} (mg g^{-1}) is the maximum amount of dye/unit weight of mixture to form a complete monolayer on the surface and k_L is the Langmuir adsorption constant. The characteristics of the Langmuir isotherm can be expressed by a dimensionless constant called the Langmuir equilibrium parameter, R_L, given in eqn. 4.

$$R_L = 1/1 + k_LC_o \quad (4)$$

The value of R_L indicates the type of isotherm either to be unfavourable ($R_L > 1$), linear ($R = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

The empirical Freundlich equation based on sorption on heterogeneous surface is given in eqn. 5

$$q_e = K_fC_e^{1/n} \quad (5)$$

where K_f and n are the Freundlich constant characteristics of the system. Eqn. 4 can be linearized in logarithmic form and Freundlich constant can be determined.

The experimental data were fitted using the Langmuir (Fig. 4) and Freundlich (Fig. 5) models.

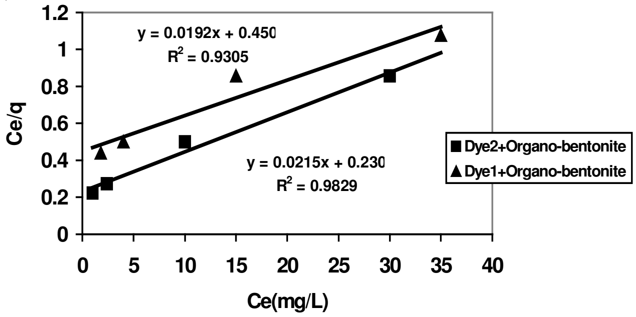

Fig. 4. Langmuir isotherm for adsorption of dyes on organo-bentonite

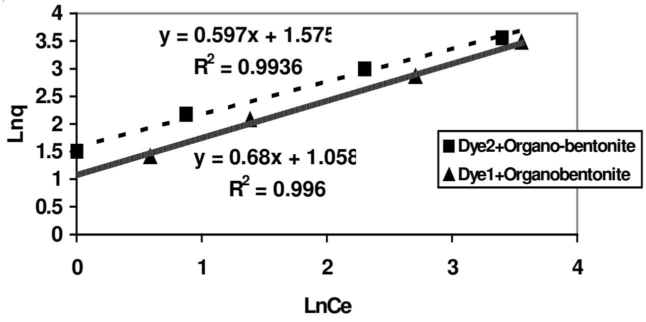

Fig. 5. Freundlich isotherm for adsorption of dye on organo-bentonite

The linear plots of C_e/q_e *versus* C_e show that the adsorption obeys Langmuir isotherm model (Figs. 3 and 4). Corresponding constants, q_{max}, k_L and R_L, were calculated from the intercepts and slopes of the plots and are presented in Table-3. R_L values between 0 and 1 for all experiment condition indicate favorable adsorption of dye onto sorbents. Linear plot of ln q_e *versus* ln C_e shows that the adsorption follows Freundlich isotherm model as well. The R^2 values (goodness of fit criterion) computed by linear regression for all types of isotherms indicate that both model can be applied to experimental data.

TABLE-3
PARAMETERS OF LANGMUIR ISOTHERM

Dye + sorbent	q_{max}	k_L	R_L	R^2
Dye1 + bentonite	15.40	0.012	0.616	0.9699
Dye2 + bentonite	21.14	0.013	0.600	0.9747
Dye1 + organo-bentonite	52.08	0.042	0.310	0.9305
Dye2 + organo-bentonite	46.51	0.093	0.176	0.9829

The effect of sorbents dose on per cent of dye removal at initial concentration of dye (50 mgL^{-1}) and 18 h contact time are shown in Figs. 6 and 7. The percentage removal of examined dyes increases with the increase in dose of adsorbent. This may be due to the increase in availability of surface active sites resulting from the increased dose and conglomeration of the adsorbent.

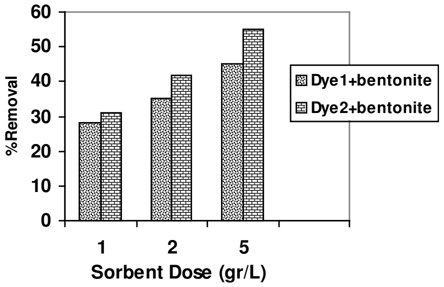

Fig. 6. Effect of sorbent dose on dye removal by bentonite

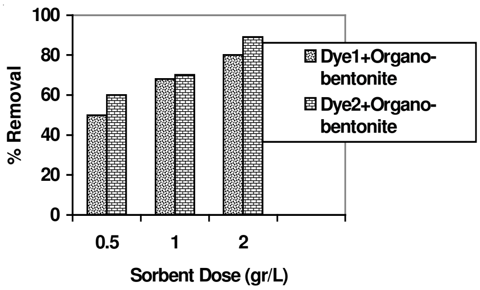

Fig. 7. Effect of sorbent dose on dye removal by organo-bentonite

Conclusion

Natural bentonite clay was modified by commercial grade alkyl dimethyl benzyl ammonium chlorides and the synthesized organo-bentonite was used for industrial dye removal from aqueous solutions. Pigment blue 60 and disperse blue 56 are found to adsorb better onto organo-bentonite than preliminary treated bentonite. The adsorption equilibrium is practically achieved in 4 h. The adsorption process is found to be a pseudo-second order kinetic. The results indicate that ADBAC-bentonite might be used as low-cost alternative sorbent for pigment blue 60 and disperse blue 56.

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