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EVALUATION OF TURKISH BENTONITE FOR REMOVAL OF DYES FROM TEXTILE WASTEWATERS

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Abstract. Removal of reactive dyes from textile industry wastewaters is a great economic and environmental challenge. In this study, systematic adsorption tests were carried out using natural and modified bentonites to remove a textile dye, Procion Navy HEXL. The results indicated an optimum at 0.1% solids concentration and 4 h of mixing time. The modified bentonite (hexadecyltrimethylammonium bromide, HTAB) had a 12-fold increase in the adsorption capacity compared to the natural bentonite. The zeta potential experiments revealed that the negative surface charge of natural bentonite at all pH values became positive upon modification with HTAB. These results clearly indicated that the negatively charged dye can adsorb onto bentonite surface via electrostatic attraction. In addition, adsorption isotherm models (Langmuir, Freundlich and Dubinin–Radushkevich) were used to analyze the adsorption in the dye-bentonite system. It is concluded that bentonite after surface modification can be conveniently used in the abatement of reactive azo dyes in textile wastewaters.

keywords: textile wastewater, dye, Procion Navy HEXL, bentonite, adsorption

1. Introduction

Wastewaters from textile industry cause considerable environmental pollution in the world. Particularly, wastewaters containing soluble dyes must be cleaned before they are discharged to nature. Therefore, textiles dyeing processes as well as the chemical content of dyeing components are very important. The dyed wastewaters consist of generally acids, bases, dissolved solid toxic compounds, and considerable colored pollutants (Armagan et al., 2004). Moreover, many dyes are toxic, and obstruct catalytic effects and also cause severe damages to the human bodies (Baskaralingam et al., 2006; Ozcan et al., 2007). While reactive dyes are fairly soluble in water, their removal from wastewater by conventional coagulation and activated sludge process is rather difficult (Ozdemir et al., 2004).

Oxidation and adsorption are two basic techniques used in the treatment of textile industry wastewater. UV/o zone and UV/H_2O_2 oxidation methods are used to make wastewater colorless (Espantaleón et al., 2003; Baskaralingam et al., 2006; Ozcan et al., 2007; Eren and Afsin, 2008; Turabik, 2008). Adsorption is an important method commonly used for cleaning of wastewater for treatment and separation of colorants in

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industrial processes (McKay, 1982). It is claimed that activated carbon and polymer resin are good but relatively expensive for the removal of chemicals from wastewater (McKay, 1982; Ozcan et al., 2007; Turabik, 2008).

Activated carbon is known to have a fairly low adsorption capacity for some reactive dyes (Juang et al., 1997). There are also a number of studies on decolorization of wastewater using cost-effective adsorbent systems, chitosan/reactive (Juang et al., 1997), montmorillonite and sepiolite/methylgreen (Rytwo et al., 2000), sepiolite/rhodamine (Arbeloa et al., 1997), and natural zeolite/basic dye (Armagan et al., 2004; Ozdemir et al., 2004; Benkli et al., 2005; Ozcan et al., 2007; Turabik, 2008). In recent years, since activated carbon adsorbent is expensive, low-cost natural clays such as sepiolite (Espantaleón et al., 2003; Ozdemir et al., 2004; Alkan et al., 2007), bentonite (Espantaleón et al., 2003; Baskaralingam et al., 2006; Ozcan et al., 2007; Eren and Afsin, 2008; Turabik, 2008), zeolite (Espantaleón et al., 2003; Baskaralingam et al., 2006; Ozcan et al., 2007; Eren and Afsin, 2008; Turabik, 2008), and montmorillonite (Wang et al., 2004) have been used directly or modified for cleaning of textile industry wastewater.

Meanwhile, the adsorption isotherm is one of the most important data to understand the mechanism of the adsorption systems. For this purpose, several isotherm models have been widely used for the systems (Espantaleón et al., 2003; Baskaralingam et al., 2006; Ozcan et al., 2007; Eren and Afsin, 2008; Turabik, 2008). For example, in our study, three important adsorption models, namely Freundlich (Freundlich, 1906), Langmuir (Langmuir, 1918), and Dubinin–Radushkevich (D-R) (Dubinin and Radushkevich, 1947) were used in the analysis of adsorption data.

The aim of this study is to examine the adsorption mechanism of reactive Procion Navy HEXL dye by natural and modified bentonites, and find out their applicability to textile waste waters. The effects of parameters such as solids concentration, mixing time, and dye concentration on the adsorption capacity of bentonite were systematically investigated. Additionally, the adsorption isotherms, Langmuir, Freundlich, and D-R, were used to find the best-fitted model for the adsorption results. The results will help provide a basis for removal of colorants through the use of bentonite.

2. Materials and methods

2.1. Materials

The bentonite sample, Na-bentonite, used for the experiments was obtained from Samaş Bentonite Company in Reşadiye-Tokat region of Turkey. The chemical analysis of Na-bentonite sample (<63 μm) was performed by inductively coupled plasma (ICP, Perkin Elmer Model 3800). The mineralogical composition of the sample was identified by XRD technique using air-dried and ethylene-glycol treated samples (Rigakudiffractometer with Cu(K_α) radiation). The chemical and mineralogical composition of Na-bentonite was given elsewhere (Bulut et al., 2009).

The bentonite sample has an average particle size (d_{50}) of 3 μm as determined by Fritsch Particle Sizer. The raw bentonite has a cation exchange capacity (CEC) of 76.45 meq/100 g whereas the purified bentonite was found to have a CEC of 99.2 meq/100 g.

A quaternary amine, hexadecyltrimethylammonium bromide (HTAB, C19H42BrN, 99% purity), purchased from SIGMA, was used for modifying the surface of bentonite. The chemical structure of HTAB and the procedure for the preparation of modified bentonite are given elsewhere (Sabah, 1998). Briefly, the modification process involves mixing of 3% solids with $3\cdot10^{-2}$ M HTAB followed by solid–liquid separation and drying. When the surface of bentonite was modified with HTAB, the clay surface was converted from polar to nonpolar properties. First, 3% bentonite was conditioned at 60ºC for 1 h in water and then treated with HTAB at 25ºC for 2 h. Distilled and deionized water with a conductivity value of $2\cdot10^{-6}$ mohms/cm was used in all experiments.

A commercial dye, Procion Navy HEXL with reactive azo group and aminochlorotriazine was used for the adsorption experiments. It contains an anionic sulfonate group. This dye is a commercial sample, and its structure is not given in the Color Index.

2.2. Methods

2.2.1. Zeta potential experiments

The zeta potential measurements of the bentonite samples were carried out with the Zeta Meter 3.0 equipped with a microprocessor unit, which automatically calculates the electrophoretic mobility of particles, and then converts it to zeta potential. First, a bentonite sample of 0.1 g was conditioned in 100 cm^3 of distilled water for 10 min. Then, the suspension was kept for 5 min to allow the large particles to settle down. Finally, the zeta potential measurements were carried out with the natural and modified bentonite samples. Each data point was taken as an average of approximately 10 measurements. All measurements were made at room temperature (22.5±1ºC).

2.2.2. Adsorption experiments

The adsorption tests were carried out using the natural and modified bentonite samples in 20 cm^3 glass vials at 0.1% solids concentration. The vials were shaken at 400 rpm using an orbital shaker (Edmund Buhler KL-2) for 4 h followed by centrifugation for 10 min. The equilibrium concentration of the dye Procion Navy HEXL was determined by UV automatic spectrophotometer (UV-2000). The samples for UV analysis were filtered to remove the suspended matters. The adsorption density was calculated by the following formula:

$$\Gamma = \frac{(C_i - C_e) \cdot V}{m1000}, \tag{1}$$

where Γ is the amount of dye adsorbed per g of adsorbent in mg/g, C_i is the initial dye concentration in mg/dm^3, C_e is the equilibrium (residual) dye concentration in mg/dm^3, V is the volume of the solution in dm^3, m is the mass of adsorbent (g).

2.2.3. Adsorption models

Langmuir, Freundlich, and D-R isotherm models, which are two-parameter equations, were used to identify the adsorption mechanism of dye-bentonite system. The Langmuir isotherm is represented as below (Espantaleón et al., 2003; Baskaralingam et al., 2006; Ozcan et al., 2007; Eren and Afsin, 2008; Turabik, 2008):

$$q_e = \frac{\mathrm{K}_L a_L C_e}{1 + a_L C_e} \tag{2}$$

where K_L is the constant of the Langmuir model related to the adsorption capacity, a_L is the constant of the Langmuir model related to the energy of adsorption.

The theoretical maximum monolayer adsorption capacity q_m (mg/g) is numerically equal to ($\mathrm{K}L/a_L$). Freundlich equation is based on the equation (Espantaleón et al., 2003; Baskaralingam et al., 2006; Ozcan et al., 2007; Eren and Afsin, 2008; Turabik, 2008):

$$q_e = \mathrm{K}_f C_e^{1/\mathrm{n}} \tag{3}$$

where K_f is Freundlich constant with indicators of adsorption capacity, n is Freundlich constant with indicators of adsorption intensity.

D–R isotherm is expressed as follows (Espantaleón et al., 2003; Baskaralingam et al., 2006; Ozcan et al., 2007; Eren and Afsin, 2008; Turabik, 2008):

$$q_e = q_m \exp\left\{ \frac{\left[RT \ln\left(1 + \frac{1}{C_e}\right)\right]^2}{\left(-2E^2\right)} \right\} \tag{4}$$

where q_m is the maximum adsorption capacity (mg/g), E is the energy of adsorption (kJ/mole).

In addition, nonlinear regression technique was performed to optimize the isotherm parameters of reactive Procion Navy HEXL dye adsorption on bentonite surface. The solver add-in function of the Microsoft Excel was used for nonlinear regression method (Corporation, 2002).

3. Results

3.1. Effect of solids concentration on adsorption

In order to obtain the optimum solids concentration for the adsorption tests with the natural bentonite sample, a series of adsorption experiments were carried out at different solid concentrations at 25 mg/dm^3 dye concentration. The conditioning time was kept at 4 h. The results from these experiments shown in Fig. 1 indicate that as the solids content is increased, the adsorption density decreases with increasing solid concentration down to 0.1% solids concentration (1 mg/g). Beyond this point, there was a slight decrease in solids concentration. According to these results, 0.1% solids concentration was chosen for further studies with the natural and modified bentonite samples.

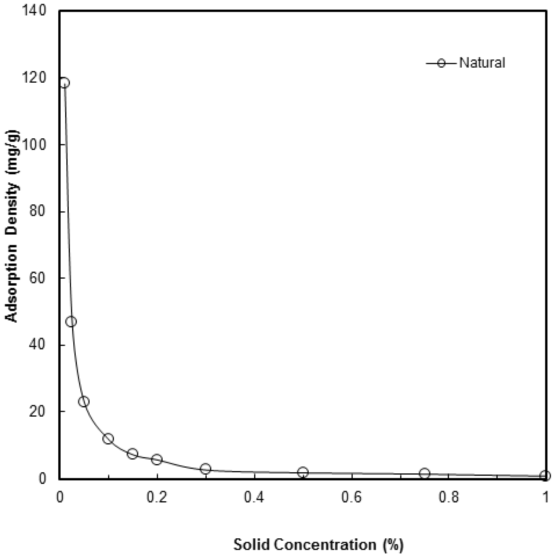

Fig. 1. Variation of adsorption of Procion Navy HEXL dye on natural bentonite with solids concentration

3.2. Effect of mixing time on adsorption

A series of adsorption experiments with the natural bentonite were also carried out as a function of time in order to find the optimum time. The experiments were carried out at an initial dye concentration of 25 mg/dm^3 and 0.1% solids concentration. As seen from Fig. 2, the adsorption density sharply increased up to 1 h, further increased with increasing the time and finally reached the plateau at 2 h. As seen from Fig. 2, even though the adsorption density reached a plateau at 2 h, 4 h of conditioning time was chosen for further studies taking into consideration some factors such as pH, concentration, and temperature etc. (Armagan et al., 2004; Ozdemir et al., 2004).

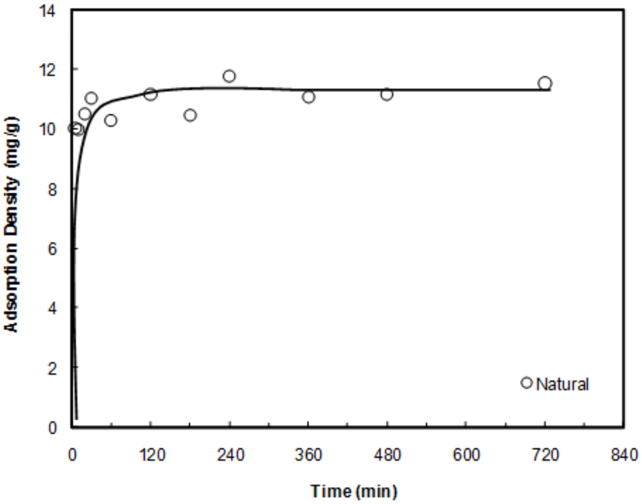

Fig. 2. Adsorption of Procion Navy HEXL dye onto natural bentonite against conditioning time

3.3. Effect of dye concentration on adsorption

The adsorption experiments were carried out with the natural and modified bentonite samples at different dye concentrations to obtain the adsorption isotherms of bentonite/dye system. The experiments were conducted at 0.1% solids concentration and mixing time of 4 h. Figure 3 shows the adsorption isotherms of dye Procion Navy HEXL on the natural and modified bentonites. As seen from Fig. 3, in the case of the natural bentonite, the adsorption density increased up to 20 mg/g, and then reached a plateau. Meanwhile, as can be clearly seen from Fig. 3, the modification of bentonite with HTAB led to about a 12-fold increase in the adsorption capacity of bentonite.

4. Discussion

Wastewaters in textile industry cause a detrimental effect to the environment, and this problem must be solved economically and efficiently. Therefore, many physical, chemical, and biological methods have been used, in the industry. However, these methods are expensive, and there is a need for low cost methods to reduce the contamination in wastewaters. For example, it has been suggested that low-cost natural clays such as bentonite (Ozcan et al., 2007; Eren and Afsin, 2008; Turabik, 2008), sepiolite (Ozdemir et al., 2004; Alkan et al., 2007), and zeolite (Armagan et al., 2003; Armagan et al., 2004; Ozdemir et al., 2004; Benkli et al., 2005) can been used either directly or after modification for wastewater treatment.

In this study, the ability of bentonite to uptake the reactive Procion Navy HEXL dye was investigated in detail, and the optimum conditions for the dye-bentonite system was obtained. The results from these studies showed that the optimum solids concentration and conditioning time was 0.1% and 4 h, respectively. These data are also in agreement with the literature. For example, Ozdemir et al. (2004) and Armagan et al. (Espantaleón et al., 2003; Baskaralingam et al., 2006; Ozcan et al., 2007; Eren and Afsin, 2008; Turabik, 2008) showed that the optimum solids concentration of sepiolite and zeolite for reactive dyes was found 4 h at 25 mg/dm^3 dye concentration. In addition, the natural bentonite was modified with HTAB to increase its adsorption capacity. The adsorption tests with the modified bentonite showed that the modification process significantly increased the uptake of the bentonite. Based on the results from batch experiments, the modified bentonite yielded 12 times more adsorption capacity than the natural bentonite. The aim is to clarify fundamental details regarding the uptake of dye molecules from wastewaters using bentonite.

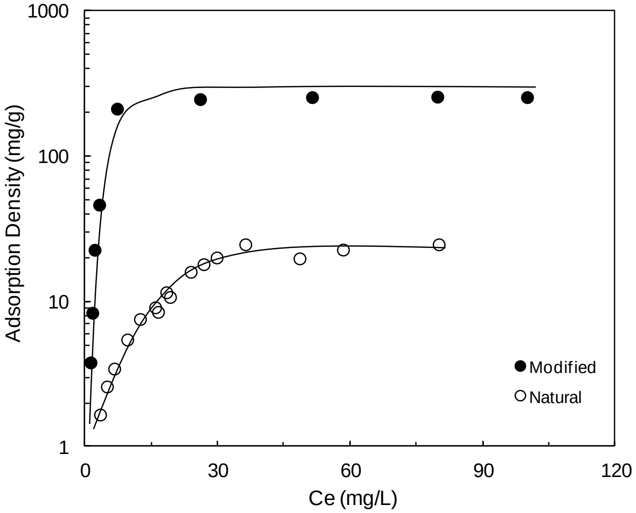

Fig. 3. Comparison of adsorption isotherms for natural and modified bentonite/Procion Navy HEXL dye

4.1. Zeta potential experiments

It is well known from the literature that zeta potential measurements are vitally important to determine the stability of clay-water system. For this reason, the zeta potential measurements with the natural and modified bentonites were carried out as a function of pH. The results presented in Fig. 4 clearly reveal that the natural bentonite was negatively charged at all pH values with no point of zero charge. On the other hand, the modified bentonite exhibited positive charges throughout the pH region (Fig. 4).

Procion Navy HEXL dye contains negative azo groups and thus exhibits negative surface charges. Since natural bentonite contains positive charges only at the edges, the overall net charge density is negative, particularly above pH 7. Adsorption of negatively charged dye molecule is weak at the natural bentonite surfaces. However, the modification of bentonite with HTAB (quaternary amine surfactant) showed a considerable increase of the adsorption density. In this way, the bentonite surfaces became hydrophobic, and the negative charges of the surfaces were neutralized (Ozdemir et al., 2004).

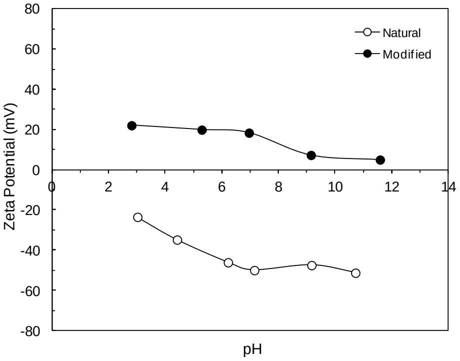

Fig. 4. Zeta potential profiles of natural and modified bentonites

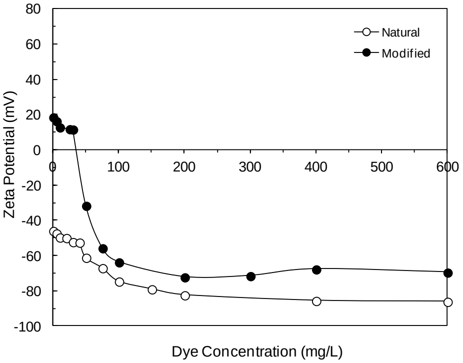

Fig. 5. Zeta potential profiles of the natural and modified bentonites vs. the dye concentration

The zeta potential measurements for natural and modified bentonites were also performed at different dye concentrations in order to understand the adsorption mechanism. The results presented in Fig. 5 show that the surface charges of the natural bentonite sample become more negative with an increase in dye concentration. This shows that the dye adsorbs on positive sites of the bentonite sample. At the same time, the positive charge of the modified bentonite decreased with increasing the dye concentration up to 25-30 mg/dm^3. Then, the surface charge sharply decreased, and became negative above 40 mg/ dm^3 dye concentration. When the dye concentration is further increased, the surface charge decreased slightly, and then reached a constant value. These results support the adsorption tests. Electrostatic attraction with negatively charged dye groups appeared to be instrumental in the uptake of dye onto the bentonite surface.

4.2. Adsorption models

The experimental data for absorbed Procion Navy HEXL dye onto natural and modified bentonites were compared using three of the two-parameter isotherm models, i.e. Langmuir, Freundlich, and D–R in order to find the best-fitted model for the data obtained. The different equation parameters and the underlying thermodynamic hypotheses of these models often provide insight into the adsorption mechanism, the surface properties and affinity of the adsorbent (Armagan et al., 2003). The isotherms obtained from the models are shown along with the isotherms from the experiments in Fig. 6. Finally, the equilibrium thermodynamic parameters were calculated for the dye-bentonite system, and the results for the isotherm constants and correlation coefficients (R^2) are presented in Table 1.

As seen from Fig. 6a, Langmuir, Freundlich, and D–R models fit very well the experimental equilibrium data for the natural bentonite. However, the Langmuir and D–R models give slightly better fitting than Freundlich model in the case of the modified bentonite (Fig. 6b). The reason for that can be attributed to the fast adsorption of dye molecules on the modified bentonite. As also seen in Table 1, all isotherms (Langmuir, Freundlich, and D-R) fit well with the experimental data (correlation coefficient R^2 = 0.975, 0.941, and 0.973) for the natural bentonite whereas the low correlation coefficient (R^2 = 0.804, 0.669, and 0.767) indicates poor agreement of isotherms with the experimental data for the modified bentonite. It may be due to the sorption that occurs at specific homogeneous sites within the adsorbent (Bouberka et al., 2006; Lian et al., 2009). Ma et al. (Espantaleón et al., 2003; Baskaralingam et al., 2006; Ozcan et al., 2007; Eren and Afsin, 2008; Turabik, 2008) found similar results, which exhibited a sharp initial rise in all the adsorbents (type I isotherm). They attributed predominant effect of strong electrostatic adsorbent–adsorbate forces of attraction, which meant a high affinity between the dye and the adsorbent surface (Ma et al., 2011).

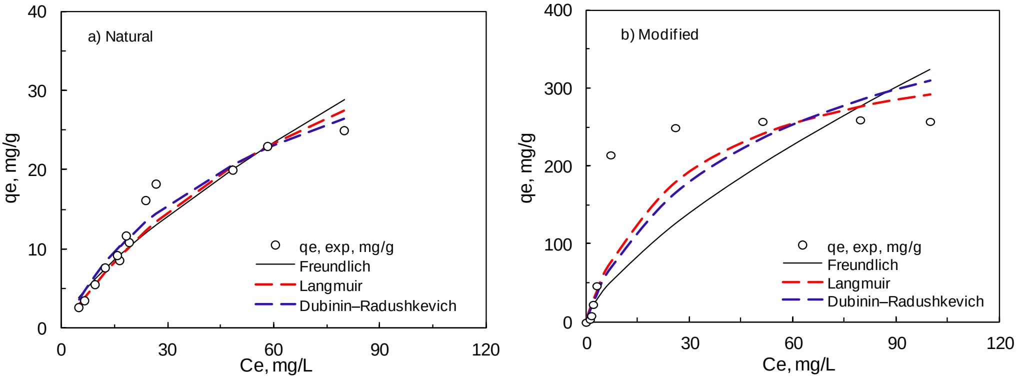

Fig. 6. Results for the adsorption models of dye-bentonite system: a) natural, and b) modified bentonite

Table 1. Parameters obtained from the adsorption models

	Langmuir				Freundlich			Dubinin–Radushkevich		
	K_L	a_L	$q_m=K_L/a_L$	R^2	K_f	1/n	R^2	q_m	E	R^2
Natural	0.784	0.018	43.747	0.975	1.161	0.728	0.941	49.758	5.644	0.973
Modified	13.103	0.035	375.163	0.804	12.947	0.699	0.669	494.804	6.463	0.767

According to Table 1, adsorption capacities were calculated from Langmuir (43.747 and 375.163 mg/g), Freundlich (1.161 and 12.947 mg/g), and D-R isotherm models (49.758 and 494.804 mg/g) for natural and modified bentonite, respectively. There are several similar studies in the literature. For example, the adsorption capacities of 98.6, 99.9, and 95.2 mg/g for Acid Yellow 194, Acid Blue 349, and Acid Red 423, respectively, on sepiolite were found to be higher than that on activated carbon (49.2, 68.2, and 26.3 mg/g) but similar to that on natural bentonite (24.9, 92.7, and 29.1 mg/g) (Espantaleón et al., 2003; Baskaralingam et al., 2006; Ozcan et al., 2007; Eren and Afsin, 2008; Turabik, 2008).

Qiao et al. (2009) measured single dye adsorption equilibrium and analyzed the experimental data with the Langmuir, Freundlich and Redlich-Peterson isotherms. Their results fit well Redlich-Peterson model and provided the best correlation of the experimental data and also the adsorption capacities estimated from the Langmuir model for AR18 and AY23 were at 69.8 and 75.4 mg/g, respectively. Ozcan et al. (Ozcan et al., 2004) compared the results of natural and modified bentonite using dodecyl trimethylammonium bromide (DTMA) for the removal of acid blue 193. The adsorption capacity of DTMA-bentonite (740.5 mg/g) was found to be about 11-fold higher than that of Na-bentonite (67.1 mg/g) at 20°C. Ozcan et al. (2007) also found out that adsorption capacity was 206.58 mg/g for DTMA-bentonite in acidic solutions for the removal of reactive Blue 19, and adsorption isotherm data were fitted to the Langmuir model.

Ma et al. (2011) emphasized that the adsorption capacity of organobentonite was affected by the surfactant alkyl chain length. The longer chain surfactant of modified bentonite shows higher adsorption capacity. As the surfactant carbon chain length decreased from C16 to C8, the adsorption capacities of Orange II decreased from 298.39 mg/g to 144.08 mg/g. The adsorption capacities of Orange G showed the same tendency (from 170.46 to 94.72 mg/g). Eren (Eren, 2009) showed that Langmuir monolayer adsorption capacities of raw and manganese oxide modified bentonite as 131 and 457 mg/g, respectively. The Langmuir model with the maximum adsorption capacity of 227.27 mg/g agreed very well with experimental data whereas Freundlich model yielded 119.40 mg/g adsorption capacity (Lian et al., 2009).

For the D-R isotherm, E (kJ/mole) gives information about the type of adsorption (physical, chemical, and ion exchange). The energy of adsorption refers to transfer of one mole of ion from the bulk to the interface. When this value of free energy is in the range of 1-8 kJ/mole, the adsorption type can be classified as physical (Helferrich, 1962). An energy range between 8 and 16 kJ/mole indicates ion exchange (Cestari et al., 2007) and when the energy is more than 16 kJ/mole the type of adsorption can be stated as chemical adsorption (Basar, 2006; Tahir and Rauf, 2006). Because the magnitude of E calculated from the D-R isotherm is lower than 8 kJ/mole for both natural and modified bentonites, the adsorption mechanism of dye onto bentonite can be described by physical interactions. Tahir and Rauf (2006) found that the adsorption free energy from D-R isotherm for uptake of Malachite Green oxalate dye on bentonite at different temperatures were between 1.00 and 1.13 kJ/mole corresponding to physical adsorption. On the other hand Eren (2009) found that adsorption energy from D-R isotherm for Crystal Violet onto raw and modified bentonite were 11.47 and 19.55 kJ/mole, the adsorption type can be explained based on ion exchange and chemical adsorption, respectively.

5. Conclusions

The adsorption of Procion Navy HEXL on the bentonite sample was systematically investigated. The results showed that while the natural bentonite has an adsorption capacity of about 20 mg/g, bentonite modified with quaternary amines significantly increased its capacity (about 12 times, 250 mg/g). The zeta potential experiments indicated that the adsorption mechanism of dye on the modified bentonite is governed by electrostatic attraction of negatively charged dye groups on the positively charged surface. Finally, the adsorption data obtained from the experiments were analyzed using the adsorption models, i.e. Langmuir, Freundlich, and D–R. The results indicate that while all three models demonstrated a good correlation for the adsorption of dye molecules on the natural bentonite, it was not so good on modified bentonite.

These results clearly showed that modified bentonite could be used for the removal of dyes in textile wastewaters due to its low cost and high yield. This will be not only a good alternative to high cost absorbents such as activated carbon and polymer resins, but also help solve environmental problems.

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