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Decolorization of Basic Textile Dyes using a Novel Adsorbent Modification Method: Ultrasonic-Acid Modification

Kalipci, E.*, Sahinkaya, S., Dortkol, M. and Aras, S.

Department of Environmental Engineering, Nevsehir Hacý Bektas Veli University, 50300 Nevsehir, Turkey

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ABSTRACT: In this study, removal of methylene blue (MB) and maxilon blue SL 200% (MB SL) dyes from aqueous solutions by using raw clay (RC) of Nevsehir (Turkey) vicinity and ultrasonic-acid modified clay (MC) was investigated. Adsorption was carried out with 500 mg/L MB and 50 mg/L for MB SL in terms of different adsorbent dosages, contact time, solution pH, temperature and stirring speed. The fitting of adsorption process with respect to Freundlich and Langmuir isotherms was examined. In this study, it was determined that the experimental data for MB dye removal by using RC (R^2= 0.9737, Q_o=3333 mg/g) and MC (R^2=0.9914, Q_o=5000 mg/g) were well fitted to Langmuir isotherm model. In addition to this, the experimental data for the removal of MB SL dye by using RC (R^2= 0.9104, K_F =19.45 mg/g) and MC (R^2=0.9933, K_F =44.62 mg/g) were well fitted to Freundlich isotherm model. As a result; it was indicated that raw clay can be used for the removal of cationic MB and MB SL dyes and ultrasonic-acid modified clay has high adsorption capacity for both of the dyes. Low-cost clay can be used for the removal of MB and MB SL dyes in preference to other adsorbents. Ultrasonic-acid modification was found as an alternative significant method for adsorbent modification.

Key words: Adsorption, Clay, Dye, Ultrasonic-acid modification.

INTRODUCTION

Dyes are widely utilized in many industries such as textiles, pulp mills, leather, dye synthesis, printing, food, and plastics. Textile industry among other sectors is ranked as high pollutant when wastewater composition and discharge volume are taken into consideration. This industrial sector especially consumes water in large amounts and results in remarkable amounts of dyed-wastewater (Dizge *et al.*, 2008). Over 100.000 commercially available dyes are discharged, and more than 7x10^5 tons are produced annually, with a considerable fraction being discharged directly in aqueous effluent (Crini, 2006). It has been estimated that 10–15% of the dye is lost in the dye effluent (Dizge *et al.*, 2008). The discharge of this wastewater not only damages the aesthetic nature of receiving water bodies, but also may be toxic to aquatic life (Allen *et al.*, 2004). Apart from this, serious environmental problems may arise from the toxic, carcinogenic and mutagenic nature of some dyes (Sponza, 2006). Wastewater containing dyes from the textile industry is very difficult to treat using conventional wastewater treatment methods, since the dyes are stable in the presence of light and oxidizing agents, and are resistant to aerobic digestion (Sun and Yang, 2003). Many techniques have been found for the removal of dye-containing wastewater, such as coagulation (Beltran-Heredia and Martin, 2008), Fenton process (Ozdemir *et al.*, 2011), electro-Fenton process (Sahinkaya, 2013), chemical or electrochemical precipitation (Alaton *et al.*, 2008), biological treatment processes (Isýk and Sponza, 2008), ozonation (Muthukumar and Selvakumar, 2006), and adsorption techniques (Kalpaklý *et al.*, 2013). In the methods such as chemical and electro-chemical precipitation, Fenton and electro-Fenton processes, chemical sludge with toxic and heavy metal content is formed. Removal of this sludge seriously increases the cost of treatment. Ozonation is a process which requires high-cost and qualified staff. In addition to this, ozone has a tendency to react with all pollutants in wastewater since it won't be selective. This will increase the need of ozone for adequate treatment efficiency and cause an increase in treatment cost. Little amount of decolorization is generally achieved by using biological processes (Gurses *et al.*, 2002). Among the existing technologies that can be used for the removal of dyes and other pollutants from wastewater (Forgacs

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*Corresponding author E-mail: ekalipci@nevsehir.edu.tr

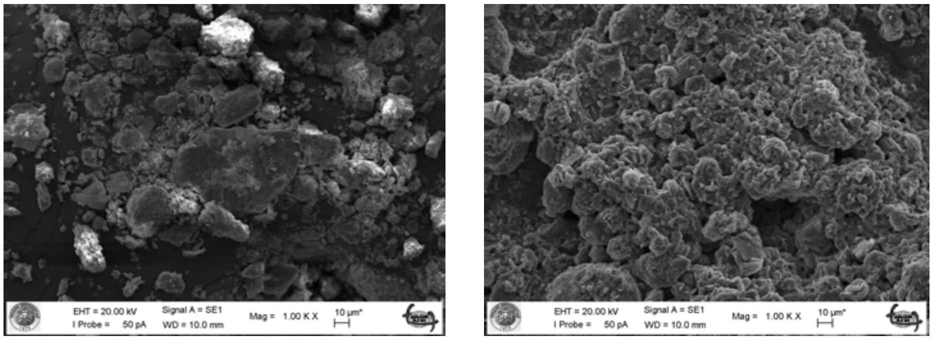
et al., 2004), adsorption is one of the most promising methods (Gupta and Suhas, 2009).

Environmental sonochemistry is a rapidly growing area, and cavitation is an effective tool for degrading different organic pollutants, including dyes (Hamdaoui *et al.*, 2008). Ultrasonication has an accelerating effect in chemical processes because of acoustic cavitation. Ultrasonic radiation creates very strong hydro-mechanical shear forces in the liquid under ultrasonic frequencies lower than 100 kHz. These forces extend the surface for adsorption by increasing and growing the pores on the surface of the adsorbent material. Thus, they improve the adsorption capacity of the material (Fernandes *et al.*, 2011; Hamdaoui *et al.*, 2008). Moreover, in the study of Hamdaoui *et al.* (2008), it was indicated that stirring speed and ultrasound caused an increase in the removal of malachite green dye.

In this study, raw clay which is abundantly found in nature and has no toxic material content is modified with ultrasonic-acid and is used as an alternative treatment material for the removal of MB and MB SL dyes from aqueous solutions. The clays from different countries are also used as adsorbents for the removal of dyes from water. These materials might improve adsorption efficiency after modification. The usage of this naturally abundant clay with this new modification method is searched for the adsorption of MB and MB SL dyes from aqueous solutions which are commonly used in textile industry all over the world.

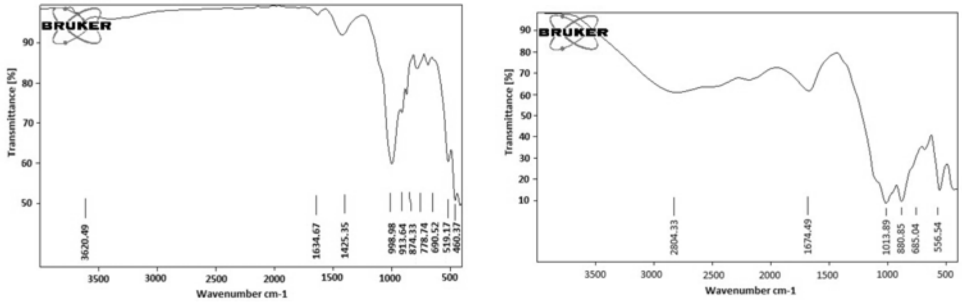
MATERIALS & METHODS

In this study, raw clay was used as an adsorbent. This raw clay was obtained from Cin stream which is approximately 4 km far away from Avanos district in Nevsehir, Turkey. Experimental studies were carried out by using raw clay (RC) and ultrasonic-acid modified clay (MC). A scanning electron micrograph (SEM) (Zeiss Evo LS 10, Germany) was used to characterize the morphology of the adsorbent. A FTIR (Fourier transform infrared spectroscopy) spectrophotometer (Bruker Vector 22, Germany) covering a wave number range of 500–3500cm^{-1} was used to identify the chemical components of the clay. The XRD examination was performed using an X-ray powder diffractometer (Bruker D8 Advance, Germany) employing Cu-Kα radiation. SEM image, FTIR analysis and XRD analysis of both clay samples are given in Fig. 1, Fig. 2 and Table 1, respectively. BET surface area and porosity of raw and modified clay samples were measured by Micrometrics FlowSorb II-2300 and Autopore II 9220 Hg Porosimeter (maximum Hg pressure 40,000 psi), respectively. The results are given in Table 2.



(a) (b)

Fig. 1. SEM image of raw clay (a) and modified clay (b)



(a) (b)

Fig. 2. FTIR analysis of raw clay (a) and modified clay (b)

Table 1. XRD analysis of raw and modified clay samples

Component of clay,%	Raw Clay	Modified Clay
SiO_2	32.27	63.9
α- Al_2O_3	4.90	4.1
ε-Fe_2O_3	3.42	1.6
CaO	26.48	-
α-SiO_2	12.80	25.4
P_2O_5	1.08	2
γ-TiO_2	2.11	3
K_2O	16.60	-
MnO	0.34	-

Table 2. BET surface area and porosity of raw and modified clay samples

BET surface area and porosity	Raw Clay	Modified Clay
BET surface area (m^2/g)	28.5	67.3
Average pore diameter (µm)	0.032	0.051
Total pore surface area (m^2/g)	26.34	62.8

The study was performed with MB and MB SL which are two types of alkaline textile dyes. Alkaline MB and commercially sold MB SL dyes were used as they are in order to prepare an aqueous solution without any further purification. MB dye was obtained from Carlo Erba company and MB SL dye was obtained commercially from the market.

50 g of sieved clay was exposed to ultrasound at 35 kHz frequency and 50 W ultrasonic power in ultrasonic water bath (Kudos, Singapore) with 6N H_2SO_4 solution of 500 mL for 2 hours. During the modification of clay, the temperature was not controlled and the clay-water mixture was stirred with a mechanical stirrer (Heidolph, Germany) at a low speed to prevent precipitation of clay in solution. At the end of 2-hour period, the mixture was filtered through a 0.45 µm membrane filter, washed until the pH of the mixture reached pH 7,and then dried at 105 ºC for 2 hours in the drying-oven. Since the particle size of adsorbent has a significant effect on the adsorption efficiency, the modified clay was also sieved through same sieves (150 and 200 micrometer), before its usage in the adsorption experiments. The solutions of MB and MB SL were prepared with ultrapure distilled water (MP Minipure Destup, Turkey). An accurately weighed quantity of MB (1g) and MB SL (1g) were dissolved in ultrapure water to prepare the stock solutions (1000 mg/L). Experimental solutions of the desired concentration were obtained by successive dilutions. All chemicals used in this study were of analytical-laboratory grade, being purchased from Merck. The batch adsorption experiments were performed to investigate the effect of experimental factors (pH, adsorbent dose, contact time and temperature) on the adsorption of MB and MB SL. The effect of experimental factors such as clay doses (15 – 30 mg and 20 – 50 mg in the adsorption tests of MB and MB SL, respectively), contact time (0 – 180 min), pH (3 – 9), and temperature (10 – 40 °C), was studied employing one factor one time approach. The pH of the solution was adjusted with 0.1 N HCl or 0.1 N NaOH by using a Hach Lange HQ30D (Germany).

Dye solutions (V = 200 mL) were taken in glass flasks (250 mL), and mixed with known amount of raw or modified clay at predefined experimental conditions. The detail of experimental conditions has been presented for each experiment in the relevant sections of Results and Discussion. The solution was then gently agitated in an cooling and shaking incubator (JSR, Japan) to achieve the equilibrium between dye-clay suspensions. After the experiment, the suspensions were centrifuged, filtered through 0.45 µm membrane filters (Millipore) to remove clay particles, and residual concentration of dye in the filtrate was determined by a UV-VIS spectrophotometer (Thermo Scientific, USA). The concentrations of residual methylene blue and maxilon blue SL were measured at λ_{max}=662 nm and λ_{max}=605 nm, respectively and were calculated according to their own calibration curve.

The adsorbed amount of MB and of MB SL at equilibrium [q_e (mg/g)] was calculated by the following equation:

$$q_e = \frac{V \cdot (C - C_e)}{W} \tag{1}$$

where C_0 and C_e are the initial and equilibrium MB and MB SL concentrations (mg/L), respectively, V is the volume of solution (L) and *W* is the dry weight of the added raw clay (g) (Alkan *et al.*, 2007; Dogan and Alkan, 2003; Zhang *et al.*, 2010).

The Langmuir isotherm presupposes monolayer adsorption onto a surface containing a finite number of adsorption sites via uniform strategies of adsorption with no transmigration of the adsorbate taking place along the plane of the surface. The linear form of the Langmuir isotherm model is described by the following equation (Weber and Digianno, 1996):

$$\frac{C_e}{q_e} = \frac{1}{Q_0 \cdot b} + \frac{C_e}{Q_0} \tag{2}$$

Where Q_0 (mg/g) and *b* (L/mg) are the Langmuir constants relating to adsorption capacity and rate of adsorption, respectively, q_e is the amount of MB and of MB SL adsorbed at equilibrium (mg/g) and C_e is the liquid-phase equilibrium concentration (mg/L) (Zhang *et al.*, 2010; Weber and Digianno, 1996).

The Freundlich adsorption isotherm is expressed by the following equation obtained on the assumption that multilayer adsorption takes place on a heterogeneous adsorbent surface (Freundlich, 1906):

$$\log q_e = \log K_F + \frac{1}{n} \cdot \log C_e \tag{3}$$

where q_e is the solid phase equilibrium concentration (mg/g), C_e is the liquid-phase equilibrium concentration (mg/L) and, while K_F and 1/n are the Freundlich constants. K_F (mg /g), is the adsorption capacity of the adsorbent (i.e. the adsorption or distribution coefficient) and represents the quantity of dye adsorbed onto the raw clay per unit of equilibrium concentration. The slope of *1/n* ranging between 0 and 1 is a measure of the adsorption intensity or surface heterogeneity, this value becomes more heterogeneous as it approaches to zero. A value for *1/n* below one indicates a normal Langmuir isotherm while *1/n* above one is indicative of cooperative adsorption (Zhang *et al.*, 2010; Fytianos *et al.*, 2000).

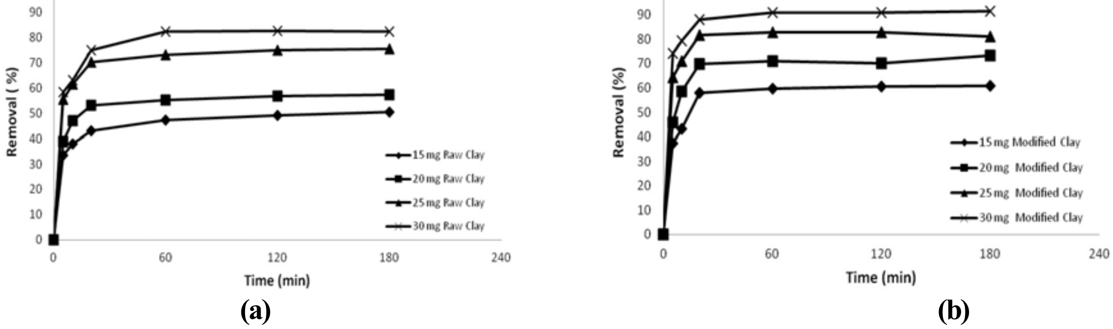
RESULTS & DISCUSSION

In this study, the adsorption capacity of raw clay was tried to improve with ultrasonic-acid modification method and the adsorption experiments were carried out using MB and MB SL dyes in the aqueous solutions in order to determine the influences of operational parameters.

The removal of MB and MB SL with RC and MC was studied with different adsorbent dosages ranging from 15 to 30 mg for MB and 20 to 50 mg for MB SL of dye solution at a constant dye concentration (500 mg/L dye concentration for MB and 50 mg/L for MB SL), stirring speed (250 rpm), pH (7) and contact time (0-180 min). For the removal of MB dye from aqueous solution, the graphs indicating time-dosage experiments with RC and MC are given in Fig. 3a and Fig. 3b, respectively. For MB removal, it was determined that the adsorption efficiencies with 15 mg, 20 mg, 25 mg and 30 mg RC at the 60th minute were found as 47.1%, 55.0%, 73.0%, 82.4%, respectively. The adsorption efficiencies by using 15 mg, 20 mg, 25 mg and 30 mg MC at the 60th minute were calculated as 59.6%, 71.0%, 82.9% and 91.0%, respectively.

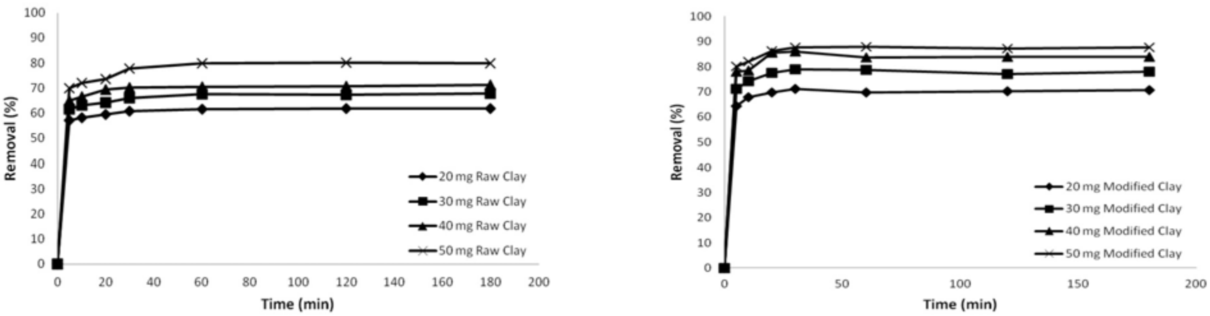
The graph indicating time-dosage study for the removal of MB SL dye from aqueous solution by RC is given in Fig. 4a and that of study performed with MC is given in Fig. 4b. For the removal of MB SL, the adsorption efficiencies by using 20 mg, 30 mg, 40 mg and 50 mg RC at the 60th minute were determined as 61.5%, 67.5%, 70.4% and 79.9%. In addition to this, the removal efficiencies for MB SL removal with 20 mg, 30 mg, 40 mg and 50 mg MC at the 60th minute were found as 69.6%, 78.7%, 83.6% and 87.9%, respectively.

In the experiments performed with raw and modified clay, it was found that the dye adsorption efficiency increased as the experimental period was prolonged. However, the dye removal efficiency was negligibly improved after 60th minute due to filling of the sorption surfaces on the clay. Raw and modified clay adsorbed MB and MB SL dyes effectively, since increase in the



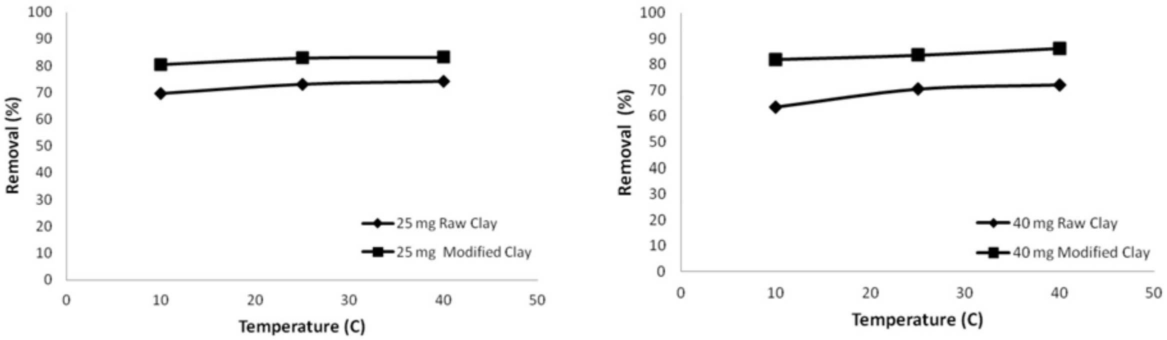
(a) **(b)**

Fig. 3. Effect of time-dosage for the removal of methylene blue by using raw clay (a) and modified clay (b)



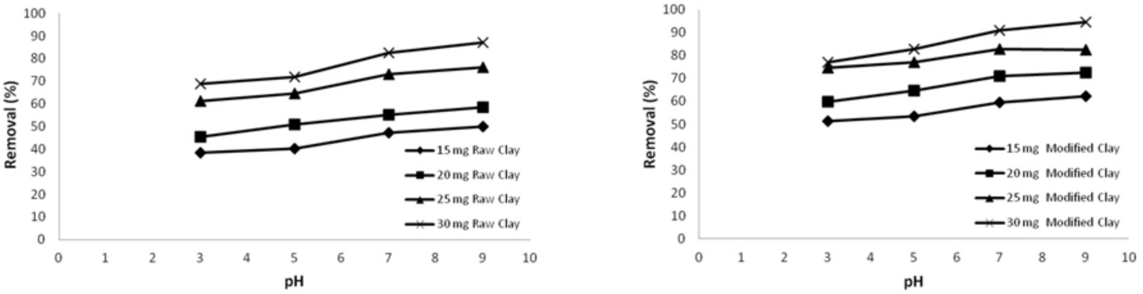
(a) (b)

Fig. 4. Effect of time-dosage for the removal of maxilon blue SL by using raw clay (a) and modified clay (b)



(a) (b)

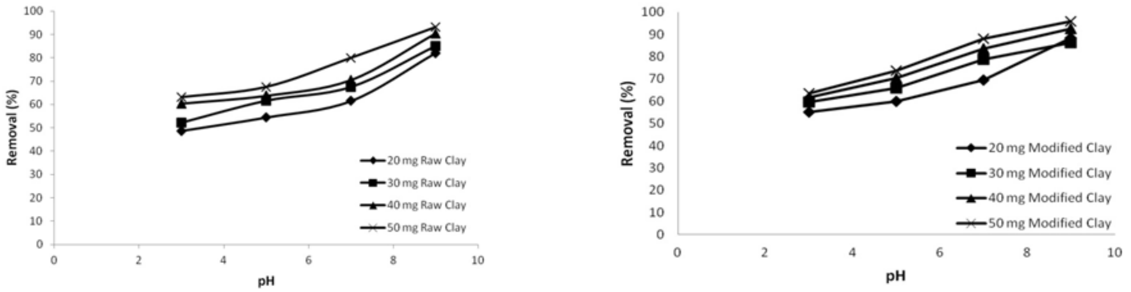
Fig. 5. Effect of temperature on the removal efficiency of methylene blue (a) and maxilon blue SL (b) by using raw clay and modified clay



(a) (b)

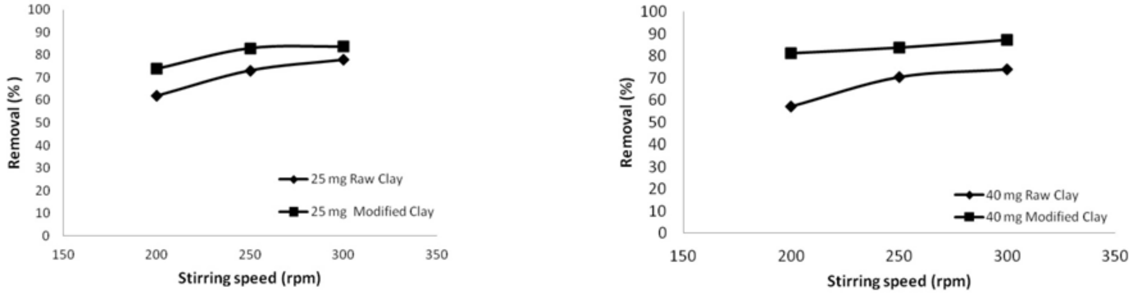
Fig. 6. Effect of pH on the removal of methylene blue by using raw clay (a) and modified clay (b) (25 ^{0}C, 250 rpm)

amount of raw clay augmented the binding sites on the surface of clay and ions. As shown in Fig. 3 and 4, the experimental studies, carried out for both dyes indicated that ultrasonic-acid modification of the clay resulted in a significant improvement in removal efficiencies because of the increased adsorption surfaces on the modified clay. As can be seen in Table 1, SiO_2 and Al_2O_3 are the major constituents of the clay with other oxides present in much smaller amounts. Hence, it is expected that either of the major oxides present in the adsorbent or their combined influence is responsible for the adsorption of MB and MB SL. Fig. 1 shows the SEM micrograph of a typical clay sample at 1000 times magnification. The raw clay particles were mostly irregular in shape and porous. Table 2 shows the BET surface area and porosity of raw and modified clay samples. The BET surface area and porosity increased after modification of the clay (Table 2). Therefore, adsorption capacity was increased by modification of the clay (as shown in Fig. 2 and Table 2). As shown in Fig. 2a and Fig. 2b, the spectra displays a number of absorption peaks, indicating the complex nature of raw clay and modified clay. The peaks at 1013–875 cm^{-1} are due to asymmetrical C–O–C



(a) **(b)**

Fig. 7. Effect of pH on the removal of maxilon blue SL by using raw clay (a) and modified clay (b) (25 ^{0}C, 250 rpm)



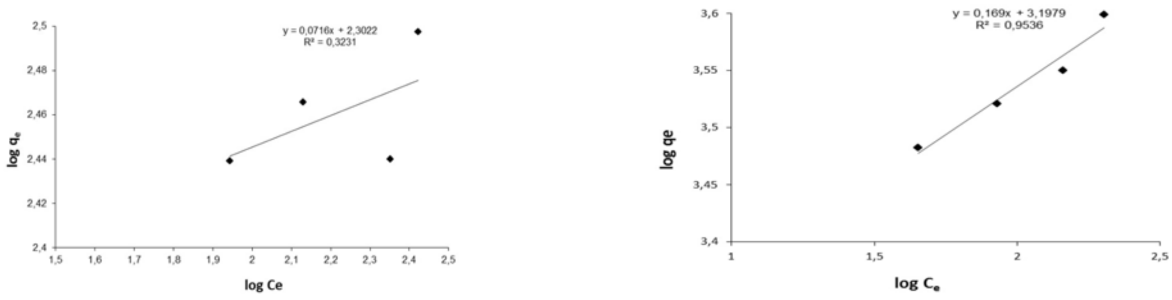
(a) **(b)**

Fig. 8. Effects of stirring speed on the removal of methylene blue (a) and maxilon blue SL (b) dyes by using raw clay and modified clay

stretching and C–H deformation. The deformation vibrations of the C–H bond in the aromatic rings give absorption bands in the range of 560–460 cm^{-1}.

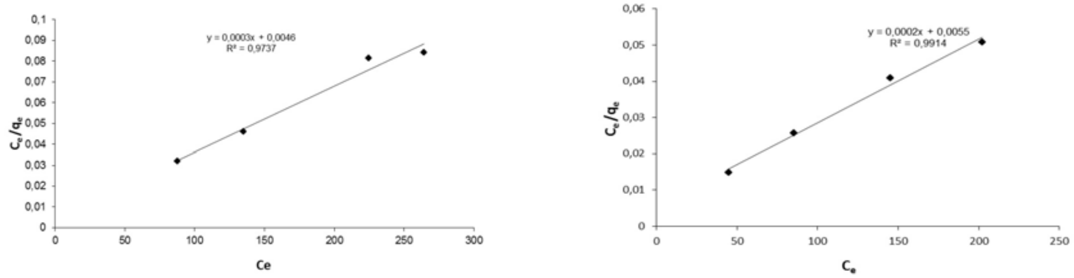
Temperature has two significant effects on the adsorption. Increasing the temperature has a known effect to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in the viscosity of the solution. In addition, changing the temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate (Alkan *et al.*, 2008; Tekin *et al.*, 2005). Therefore, effect of temperature on the removal of dyes was investigated at three different temperatures, i.e. 10°C, 25°C and 40°C. In the experiments performed with RC and MC samples, the graphs indicating the effect of ambient temperature on the removal of MB dye and MB SL dye are given in Fig. 5a and Fig. 5b, respectively. When Fig. 5a and Fig. 5b are taken into consideration, it was observed that increase in temperature did not result in an expected increase in adsorption efficiency for both of the dyes but resulted in a little increase in the efficiency. The adsorption capacity increased by the increase in temperature may cause an increase in chemical potential of dye molecules adsorbed on the surface of the clay. For this reason, 25^{0}C temperature was found suitable for the determination of optimum temperature value since it is close to normal conditions. It was determined that MC usage increased the removal efficiency of MB dye about 13% and that of MB SL dye about 18% at 25^{0}C when compared to RC usage.

Removal efficiency has been strongly affected by the pH of the solution in adsorption studies. Since pH is an important parameter affecting the adsorption capacity (Zhao and Liu, 2009; Seki and Yurdakoc, 2006), the adsorption efficiencies at pH 3-5-7-9 for MB and MB SL dyes were investigated at 25 ^{0}C and 250 rpm stirring speed in this study. In the experiments carried out for the removal of MB and MB SL dyes from aqueous solutions by using RC and MC, the graphs indicating the effect of pH are given in Fig. 6 and Fig. 7, respectively. As it can be seen from the graphs, increasing the pH values resulted in an increase in removal efficiencies for adsorption of MB and MB SL dyes. These graphs illustrate that the adsorption increases with increasing pH because the electrostatic attraction is happened between the dye and the negatively charged clay surface due to the deprotonation of the terminal OH^{-} groups at the edges of the clay minerals. As the pH increases from 5 to 9, the number of ionisable sites on clay enhances in



(a) **(b)**

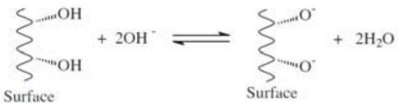
Fig. 9. Freundlich adsorption isotherm of methylene blue on raw clay (a) and modified clay (b) at 25 ^{0}C (250 rpm, pH 7)



(a) **(b)**

Fig. 10. Langmuir adsorption isotherm of methylene blue on raw clay (a) and modified clay (b) at 25 ^{0}C (250 rpm, pH 7)

accordance with Eq. (4) (Demirbas and Alkan, 2014):

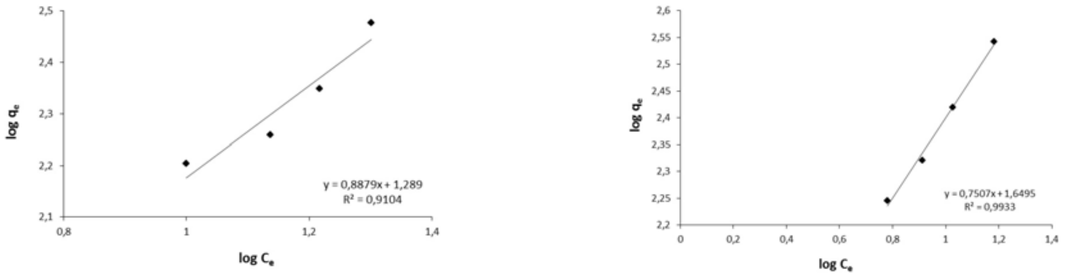


(4)

A similar effect has been reported for the adsorption of basic dye from aqueous solution onto bentonite (Gok *et al.*, 2010) and for methyl violet adsorption on perlite (Dogan and Alkan, 2003).

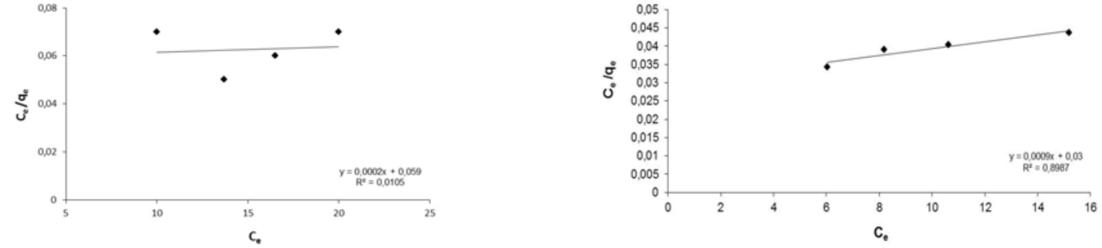
Since adsorbent material might cause a decrease in the removal efficiency by precipitating at lower speed in the contact of adsorbent with adsorbate material, the effect of stirring speed on the removal efficiency was investigated in this study. The experiments for 200 mL 500 mg/L MB dye concentration were performed at 25 ^{o}C, for 60 minutes, with 25 mg RC and MC amounts by varying stirring speeds such as 200 rpm, 250 rpm and 300 rpm (Fig. 8). For 200 mL 50 mg/L MB SL dye solution, the experiments were carried out at 25 ^{0}C, for 60 minutes, with 40 mg RC and MC by varying stirring speeds such as 200 rpm, 250 rpm and 300 (Fig. 8). For these dye solutions, it was determined that increasing the stirring speed resulted in an increase in the removal efficiency by using both RC and MC. It was also indicated that a little increase was observed above 250 rpm and 250 rpm was selected as the most suitable stirring speed for the removal of MB and MB SL dyes. Stirring is an important parameter in adsorption phenomena, influencing the distribution of the solute in the bulk solution and the formation of the external boundary film. This can be explained by the fact that increasing the stirring speed reduces the film boundary layer surrounding the particles, thus increasing the external film transfer coefficient, and hence the adsorption capacity (Crini *et al.*, 2007). McKay (1982) reported that the rate of dye removal was influenced by the degree of stirring and the uptake increased with stirring rate. The degree of stirring reduced the boundary layer resistance and increased the mobility of the system. A stirring speed of 250 rpm was found to be optimum.

Adsorption isotherms describe how dyes interact with adsorbent materials and are very important for design of adsorption system (Tehrani-Bagha *et al.*, 2011). An adsorption isotherm is characterized by certain constant values, which express the surface properties and affinity of the adsorbent and can also be used to compare the adsorptive capacities of the adsorbent for different pollutants (Malkoc and Nuhoglu, 2007). Various isotherm models have been reported in the literature (De and Basu, 1998). In this study, the fitting of experimental equilibrium data for



(a) **(b)**

Fig. 11. Freundlich adsorption isotherm of maxilon blue SL on raw clay (a) and modified clay (b) at 25 ^{0}C (250 rpm, pH 7)



(a) **(b)**

Fig. 12. Langmuir adsorption isotherm of maxilon blue SL on raw clay (a) and modified clay (b) at 25 ^{0}C (250 rpm, pH 7)

the removal of MB and MB SL dyes by using RC and MC was investigated in terms of Langmuir and Freundlich isotherm models. In order to evaluate the ability of the models to describe the adsorption process, the correlation coefficients (R^2) were calculated.

According to the data obtained from the experiments, the graphs of Freundlich and Langmuir isotherms for the removal of both dyes by using RC and MC are given in Fig. 9 to Fig. 12. It was found that the experimental data of MB dye removal by using RC (R^2= 0.9737, Q_o=3333 mg/g) and MC (R^2=0.9914, Q_o=5000 mg/g) well fitted to Langmuir isotherm model. Moreover, the experimental data of MB SL dye removal by using RC (R^2= 0.9104, K_F =19.45 mg/g) and MC (R^2=0.9933, K_F =44.62 mg/g) well fitted to Freundlich isotherm model. For both MB and MB SL dyes, the adsorption capacity of experiments performed by using MC substantially increased when compared to that of experiments carried out by RC. Thus, it was determined ultrasonic-acid modification is a significant alternative method for adsorbent modification.

CONCLUSIONS

Naturally abundant mixed clay for the removal of cationic dyes (MB and MB SL) from aqueous solutions was investigated as its raw and ultrasonic-acid modified forms in terms of different adsorbent amount, contact time, solution pH, temperature, stirring speed and adsorption isotherms. The results are summarized as follows:

The clays can be used as an adsorbent for the removal of MB and MB SL from its aqueous solutions. The experimental studies indicated that raw clay might be used as an alternative adsorbent for the removal of MB (Q_o=3333 mg/g) and MB SL (K_F =19.45 mg /g) dyes. It was also determined that it became an effective adsorbent by increasing $Q_o$value from 3333 mg/g to 5000 mg/g after modification especially for the removal of cationic methylene blue dye. For the removal of MB SL dye, on the other hand, the adsorption capacity of raw clay increased from K_F =19.45 mg/g to 44.62 mg/g. Ultrasonic-acid modification substantially increased the adsorption capacity of clay. The amount of dyes adsorbed was found to vary with initial solution pH, stirring speed, temperature, contact time, and adsorbent dose. It had fast adsorption rate and the equilibrium was achieved within only 60 min. The adsorption of MB by the raw clay and modified clay fits the Langmuir equilibrium isotherm. Fitting of the results to Langmuir isotherm indicates homogeneous and a single layer adsorption. The adsorption of MB SL by the raw clay and modified clay fits the Freundlich equilibrium isotherm. Fitting of these results to Freundlich isotherm, on the other hand, indicates heterogeneous and multi-layer adsorption. The adsorbent used has significant advantages such as being easily available, locally applicable and having low-cost. These clays can be put to good use as an adsorbent for removal of color from industrial and other effluents.

ACKNOWLEDGEMENTS

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