Investigation of the Factors Affecting the Removal of an Acid Dye from Aqueous Solution by Adsorption Using Bentonite and Sepiolite

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ABSTRACT: The effects of some factors on the adsorption of an Acid dye (Acid Blue 193, AB 193) from aqueous solution onto bentonite and sepiolite samples were studied. These factors were saturation of the samples with cations (Na^+ and Ca^{2+}), the pH and the ionic strength of the dye solution. The Langmuir and Freundlich adsorption models were used to describe the equilibrium isotherm and determine the isotherm constants for each of the samples. The Langmuir model agreed very well with the experimental data. Cation saturation led to an increase in the adsorption capacities of the samples. In addition, the adsorption capacities decreased with increasing pH of the dye solution and increased with increasing ionic strength. The maximum adsorption capacity of both the bentonite and sepiolite samples towards the cationic dye Methylene Blue (MB) was higher than that towards the anionic dye AB 193.

1. INTRODUCTION

Standard procedures for the use of Reactive dyes for dying purposes require the use of high amounts of water, salt and alkali which, in turn, lead to very large volumes of effluent. Pre-treatment of a fabric should lead to complete elimination of salt and alkali, lower water volumes and reduced process times. For these reasons, the pre-treatment method employed plays an important role in the dyeing process.

In a widely used pre-treatment method for dyeing processes, 1:2 metal complexes of Acid dyes play an important role. Such complexed dyes furnish a wide range of shades and display very high light fastness and good wash fastness on polyamide substrates such as wool, nylon and silk (Blackburn and Burkinshaw 2002). Such applications have led to the extensive use of 1:2 metal complex dyes in dyeing processes and this, in turn, has led to a simultaneous increase in effluents containing these dyes. The removal of colours from effluents arising from the use of metal complex dyes, e.g. Acid Blue 193 (AB 193), Acid Black 210, Crystal Violet and Reactive Black, is currently a major problem for environmental managers.

Of the numerous techniques employed for decolorizing, adsorption is the procedure of choice and gives the best results for the removal of different types of colouring materials (Nigam *et al*. 1996; Derbyshire *et al*. 2001; Ho and McKay 2003; Jain *et al*. 2003). The adsorption process has an edge over other removal methods because of its clean, sludge-free operation which leads to the complete removal of dyes even from dilute solutions. Adsorption is a physicochemical process in which dissolved molecules are attached to the surface of an adsorbent by physical/chemical

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forces. Activated carbon is the most popular adsorbent for such adsorption processes since it has a high surface area and a high associated adsorption capacity. However, its regeneration is difficult and expensive, and consequently the need for an alternative low-cost readily available adsorbent has encouraged the search for new adsorbents (Montanher *et al*. 2005). In this context, natural clays such as sepiolite, kaolinite, montmorillonite, smectite and bentonite are under consideration as alternative low-cost adsorbents for dye removal from wastewater (Ogawa *et al*. 1996; Arbeloa *et al*. 1997; Harris *et al*. 2001; Rytwo *et al*. 2002; Armağan *et al*. 2003; Özcan *et al*. 2004a,b; Özcan and Özcan 2004; Wang *et al*. 2004). Although possessing a lower adsorption capacity than activated carbon, natural clays are less expensive and much more abundant materials. The use of clay for decolorizing and for refining oils, fats and waxes has also been widely reported (Breen 1991; Juang *et al*. 1997; Hsu *et al*. 1997; Özcan *et al*. 2006).

Bentonite consists of a mixture of minerals, with montmorillonite being an important component but with quartz and other minerals present in substantial quantities. Bentonite is an expandable type of clay with a layered structure in which each layer has a small net negative charge due to the isomorphous substitution of ions in the framework. This charge is compensated by interlayer hydrated cations which are known as exchangeable cations. It is well known that a wide variety of organic molecules can intercalate in the interlayer regions of expandable clays (Rodriguez-Sarmiento and Pinzon-Bello 2001).

Sepiolite is a member of the phyllosilicate group of clay minerals which have peculiar surface properties and have generated important industrial interest due to their high sorption capacities. Its structure is quite different from that of smectites. Thus, the fundamental structural unit of sepiolite consists of two layers of tetrahedra and one layer of octahedra which are in the form of ribbons rather than sheets. These ribbons are linked to form an open cavity similar to that found in zeolites. In this structure, the linked Si–O chains face each other between adjacent continuous oxygen sheets. The sheets formed by the apices of the tetrahedra are completed by OH^- groups and Mg^{2+} ions in octahedral coordination which tie the sheets together. Both arrangements leave channels in the structure between and parallel to the ribbons. The exposed OH^- groups at the edges of the ribbons are neutralized by bound hydroxonium (H_3O^+) groups. The channels may be penetrated by water molecules, which are designated as zeolitic water (Santaren *et al*. 1990).

Sepiolite and bentonite are employed extensively as adsorbents in industrial applications. They also exhibit high capacities towards the removal of heavy metal ions and have been employed for wastewater treatment. The sources of the raw materials are also abundant and their relatively low costs guarantee their continued utilization in the future. Most of the world reserves of sepiolite and bentonite minerals are to be found in Turkey (Balcı and Dinçel 2002). These properties and advantages of the minerals are of great commercial interest in many areas and, as a consequence, they have been the subjects of extensive study.

Several factors influence the extent to which ions are adsorbed onto clays, including the degree of loading, the presence of ligands, complex formation, the pH of the aqueous solution in contact with the clay and the salt concentration. In the present study, the removal of Acid Blue 193 (AB 193) from aqueous solutions by sepiolite and bentonite has been examined by batch adsorption techniques. These adsorbents have also been shown to be effective and economical materials for the adsorption of AB 193 from aqueous solutions. The fit of the experimental data by the Langmuir and Freundlich adsorption isotherms was also examined. The common Langmuir equations were found to fit the equilibrium isotherm. The effects of saturation, pH and ionic strength on the adsorption of the anionic dye were also studied and the adsorption capacities of sepiolite and bentonite towards anionic and cationic dyes compared.

2. EXPERIMENTAL

2.1. Materials and methods

2.1.1. Materials

The silicate samples used as adsorbents were bentonite obtained from the Uşak region and sepiolite from the Sivrihisar/Eskişehir region. The samples are referred to below as UB and SS, respectively. Both were dried for 24 h at 105ºC and then passed through a 200-mesh sieve.

The cation-exchange capacities (CEC) of the samples were determined via saturation with NH_4^+ ions using Kjeldhal distillation (De *et al*. 1974). The values thus determined for bentonite and sepiolite were 32.35 mequiv/100 g and 6.62 mequiv/100 g, respectively.

The corresponding samples saturated with Na^+ and Ca^{2+} cations were obtained through the use of 1 N sodium and calcium chloride solutions as described by Rich (1961). The pH values of the solutions were adjusted using dilute buffer solutions as described earlier (Bilgiç 2005). Such pH measurements were made using a Hanna HI 8314 pH meter equipped with a combined electrode. The effect of ionic strength on the adsorption capacities of the samples towards Acid Blue 193 (AB 193) was investigated using KCl and $NaNO_3$ solutions whose concentrations ranged from 0.05 M to 0.5 M. In all cases, the samples were stirred mechanically for 48 h and then filtered through a white-band filter paper. The resulting residues were rinsed continuously with distilled water until they were free from chloride ions as demonstrated by the silver nitrate test.

Chemical analysis data relating to the samples are listed in Table 1. The detailed procedures regarding thermal analysis of the samples have been described earlier (Bilgiç 2005).

Synthetic textile dye AB 193 (Isolan Dark Blue 2-SGL) was used without further purification. The chemical structure of AB 193 is depicted in Figure 1.

TABLE 1. Chemical Analyses of Samples Studied

Content (%)	UB (Bentonite)	SS (Sepiolite)
SiO_2	64.94	49.00
Al_2O_3	16.93	0.41
Fe_2O_3	1.95	–
CaO	0.72	–
MgO	0.65	24.30
P_2O_5	0.27	–
K_2O	1.60	–
Na_2O	0.44	0.02
SO_3	0.62	0.02
Cl	0.001	–
TiO_2	0.62	–
SrO_2	0.08	–
Mn_2O_3	0.07	–
Loss on ignition	11.09	26.18

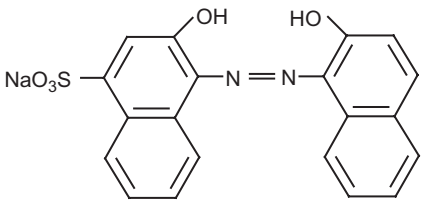


Figure 1. Chemical structure of AB193.

2.1.2. Adsorption studies

Known volumes (50 mℓ) of aqueous systems of AB 193 of known initial concentration (600 ppm) were added to varying amounts of adsorbents (0.05–0.5 g) contained in volumetric flasks. The resulting suspensions were shaken mechanically whilst being maintained in a thermostatted bath. Analytical determinations of the amounts of AB 193 present in the various solutions after equilibration (48 h at 25ºC) were performed using a Shimadzu-120-01 spectrophotometer, with optical densities being measured at 609 nm corresponding to the maximum absorption peak of AB 193. The amounts of AB 193 adsorbed were calculated from the difference between the initial and equilibrium concentrations.

3. RESULTS AND DISCUSSION

3.1. Adsorption isotherms

Several models for describing experimental adsorption isotherm data have been published in the literature. Of these, the Langmuir and Freundlich models are those most frequently employed. In the present study, both models have been employed to describe the relationship between the amounts of AB 193 adsorbed and its equilibrium concentration in solution.

The Langmuir adsorption isotherm assumes that adsorption takes place at specific homogeneous sites on the adsorbent surface and has been applied successfully in many monolayer adsorption processes. The linear form of the Langmuir isotherm equation may be represented by the following equation (Langmuir 1918; Chiron *et al*. 2003; Prado *et al*. 2004):

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \quad (1)$$

where C_e is the equilibrium concentration of solute remaining in the solution, q_e is the quantity of solute adsorbed per unit weight of adsorbent (surface excess) and q_{max} and K_L are constants arising from the Langmuir equation. These constants are called the adsorption capacity (maximum surface coverage) and the bonding energy, respectively.

The magnitudes of these constants may be obtained from the slope and intercept, respectively, of the plots arising from the application of the linear version of the Langmuir equation to the experimental data obtained. Such straight lines were fitted via an application of the method of least squares to the data, the slope of the regression line being $1/q_{max}$ while the intercept is $1/q_{max}K_L$. The linear regression lines obtained had high correlation coefficients (r^2), indicating a good fit to the Langmuir equation.

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. The linear form of this equation may be written as (Freundlich 1906):

$$\ln q_e = \ln K_F + 1/n \log C_e \quad (2)$$

where K_F and n are the Freundlich adsorption isotherm constants, being indicative of the extent of adsorption and the degree of non-linearity between the solution concentration and adsorption, respectively. The plot of ln q_e versus ln C_e for the adsorption of AB 193 onto sepiolite and bentonite was employed to generate the intercept value (K_F) and the slope (1/n).

The Langmuir isotherms arising from the experimental data for the adsorption of AB 193 onto the natural and saturated samples are depicted in Figure 2. The Langmuir and Freundlich parameters for the adsorption of AB 193 are tabulated in Table 2, together with the correlation coefficients (r^2) which provide the goodness-of-fit criteria.

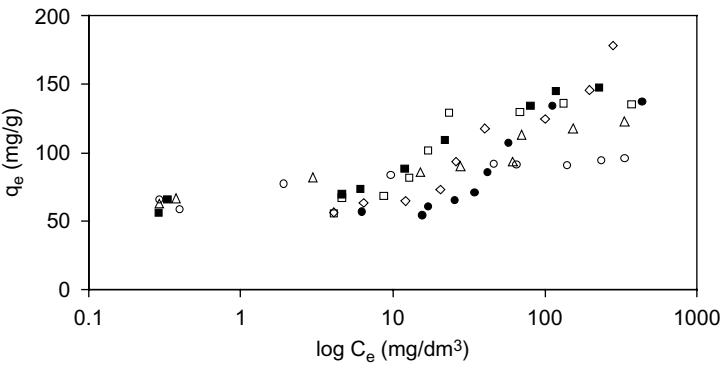


Figure 2. Langmuir isotherms for the adsorption of AB 193 onto various bentonite (UB) and sepiolite (SS) samples. Data points refer to the samples studied as follows: UB, natural (○); SS, natural (□); UB saturated with Na^+ ions (●); UB saturated with Ca^{2+} ions (△); SS saturated with Na^+ ions (■); SS saturated with Ca^{2+} ions (◇).

TABLE 2. Langmuir and Freundlich Isotherm Constants for the Adsorption of AB 193 onto the UB and SS Samples Studied

Adsorbents	Langmuir				Freundlich		
	q_{max} (mg/g)	K_L (dm^3/mg)	r_L^2	R_L	n	K_F (dm^3/g)	r_F^2
UB	95.24	0.56	0.9996	0.003	16.26	4.23	0.8966
SS	136.98	0.18	0.9995	0.009	4.90	3.90	0.7852
UB (Na^+)	144.92	0.04	0.9954	0.04	3.65	3.38	0.8453
UB (Ca^{2+})	123.45	0.16	0.9968	0.01	11.01	4.26	0.9372
SS (Na^+)	149.25	0.19	0.9982	0.008	6.79	4.17	0.9067
SS (Ca^{2+})	178.57	0.04	0.9778	0.04	3.65	3.59	0.9511

The values listed in Table 2 show that the experimental data were described more suitably by the Langmuir model rather than the Freundlich model. This is in accordance with the shapes of the sorption isotherms, which corresponded to type L2 (Langmuir type) in the Giles classification system (Giles *et al*. 1960) for the adsorption of a solute from its solution.

The essential parameters of the Langmuir isotherm can be expressed in terms of a dimensionless separation factor (equilibrium parameter), R_L, as defined by McKay *et al*. (1989):

$$R_L = \frac{1}{1 + K_L C_0} \quad (3)$$

which indicates the shape of the isotherm. Here, K_L is the Langmuir constant and C_0 is the highest initial dye concentration employed. The value of R_L calculated from the above equation is included in Table 2. The parameter indicates the type of isotherm as being irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavourable ($R_L > 1$). For the isotherms arising from the adsorption of AB 193 onto the clay samples studied, the value for this parameter was between 0 and 1, indicating that the adsorption process was favourable.

3.2. Ion exchange

Ion-exchange processes are equilibrium processes. To simplify matters, it can be said that the occupation of a cation-exchanger depends on the kind and concentration of cation available for the exchange. Furthermore, both the sizes of the cations and the number of positive charges associated with them are also important. Thus, the divalent calcium ion (Ca^{2+}) is more readily exchanged relative to the univalent sodium ion (Na^+) (Egloffstein 2001).

The isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedral layer and of Mg^{2+} for Al^{3+} in the octahedral layer of bentonite results in the generation of a net negative surface area charge. This charge imbalance is offset by exchangeable cations (Na^+ and Ca^{2+}, etc.) at the bentonite surface. The layered structure of the clay expands after wetting; in addition, Na^+ and Ca^{2+} ions are strongly hydrated in the presence of water, resulting in a hydrophilic environment at the bentonite surface (Shen 2001).

Sepiolite has silanol groups on its external surface. These are usually accessible to organic species since they act as neutral adsorption sites. In addition, isomorphic substitution in the tetrahedral sheet of the lattice mineral, such as Al^{3+} for Si^{4+}, leads to the formation of negatively charged adsorption sites. Such sites are occupied by exchangeable cations that compensate for the electrical charge (Rytwo *et al*. 2002).

3.3. Effect of cation saturation

Saturation of natural bentonite and sepiolite with Na^+ and Ca^{2+} ions increases their adsorption capacities compared with the natural samples. Thus, saturation with Na^+ ions leads to an increase in the adsorption capacity of 52% for bentonite and 9% for sepiolite, while saturation with Ca^{2+} ions leads to corresponding increases of 30% and 30%, respectively. The highest increase found for Na^+ ion-saturated bentonite was attributed to the enhanced swelling properties of the resulting material in water. This leads to separation of the montmorillonite sheets through the penetration of water molecules into the interlayer region with consequent swelling. Because individual sheets within the crystal structure can be separated in bentonites, both the external area and the internal surface area are available for adsorption. This property is most clearly observed with

Na^+ ion-saturated bentonites. Bouberka *et al*. (2005) and Özcan *et al*. (2004a) have reported that saturation with Na^+ ions increases the adsorption capacity of bentonite towards dye molecules. This is because the increased amount of Na^+ ions in the clay relative to Ca^{2+} ions results in greater dispersion, which in turn enhances the amount of dye adsorbed.

3.4. Effect of pH value

The measured adsorption spectra of AB 193 solutions prepared at different buffered pH values indicate that the value of the maximum absorbance is unaffected by changes in the pH value. Similar results have also been reported by Kumbasar *et al*. (2007) who showed spectrophotometrically that the values of λ_{max} and A_0 were the same for AB 193 solutions irrespective of whether the latter had been buffered at pH values of 3, 5 and 8, respectively.

The pH value is a very important factor in any adsorption process. In the present study, experiments were performed using various initial pH values within the range 2–11 in order to study the influence of pH on the adsorption capacities of bentonite and sepiolite. The pH values of the solutions were adjusted using dilute buffer solutions and were as tabulated in an earlier study (Bilgiç 2005).

As shown by the data depicted in Figure 3, the uptake of AB 193 decreased as the pH value increased. Under these circumstances, the positive charge on the oxide or at the solution interface decreased so that the adsorbent surface appeared to be negatively charged. In contrast, the lower adsorption capacity at higher pH values (i.e. under basic conditions) could be due to the abundance of OH^- ions on the surface resulting in a consequent ionic repulsion between the negatively charged surface and the anionic dye molecules. There are also no exchangeable anions on the outer surface of the adsorbent at higher pH values and consequently the adsorption capacity decreases (Namasivayam *et al*. 2002; Özacar and Şengil 2003). Similar results concerning the effect of pH on anionic dye adsorption have been reported in the literature (Özcan *et al*. 2004a, 2006; Alkan *et al*. 2004). The maximum removal extent of AB 193 from aqueous solution with bentonite and sepiolite occurred under acidic conditions at a pH value of 2. It was observed that the adsorption is highly dependent on the pH value of the solution, which affects the surface charge on the adsorbent and the degree of ionization and speciation of the adsorbate. At lower pH values, more protons become

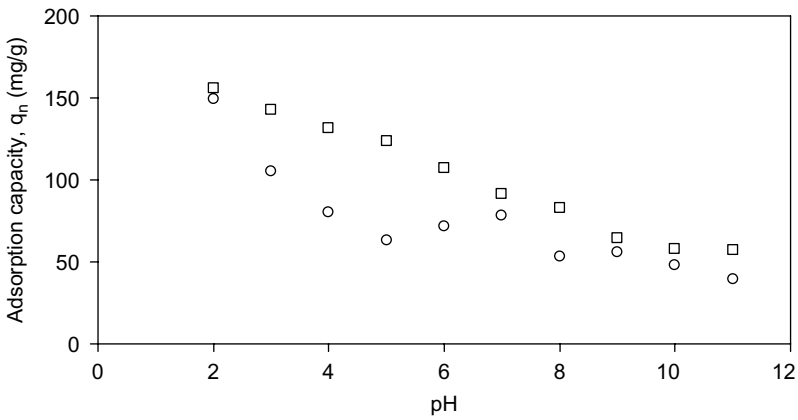


Figure 3. Influence of the pH value of the solution on the adsorption capacity of UB (○) and SS (□), respectively.

available, thereby increasing the electrostatic attraction between the negatively charged dye anions and the positively charged adsorption sites and causing an increase in dye adsorption.

The surface is positive charged at low pH where reaction (4) predominates, and is negative at higher pH when reaction (5) takes over, where S represents the active surface functional groups:

$$S\text{–}OH + H^+ \rightleftharpoons S\text{–}OH_2^+ \quad (4)$$

$$S\text{–}OH + OH^- \rightleftharpoons S\text{–}O^- + H_2O \quad (5)$$

As the pH of the dye solution diminishes below 2, the association of the dye anions with more positively charged clay surface occurs more readily because of the increasing number of $S\text{–}OH_2^+$ groups (Alkan *et al*. 2004):

$$S\text{–}OH_2^+ + dye^- \rightleftharpoons S\text{–}OH_2^+dye^- \quad (6)$$

At strongly acidic pH values, significant electrostatic attraction exists between the positively charged surface of the adsorbent and the Acid dye anions. As the pH of the system increases, the number of negatively charged sites increases relative to those of positively charged sites. This leads to increasing electrostatic repulsion between the negatively charged surface sites on the adsorbent and the dye anions, thereby reducing the extent of adsorption. In addition, the presence of excess hydroxide ions competing with the Acid dye anions for adsorption sites at alkaline pH values leads to a further reduction in the extent of adsorption.

3.5. Effect of ionic strength

To study this effect, experiments were performed using solutions with different ionic strengths within the range 0–0.5. Ionic strength affects the activity coefficients of OH^- and H_3O^+ ions, and more specifically those of adsorbable dye ions. As can be seen from the data recorded in Figure 4, the increasing ionic strength in the solution led to an increase in the adsorption of AB 193 onto the bentonite and sepiolite samples studied.

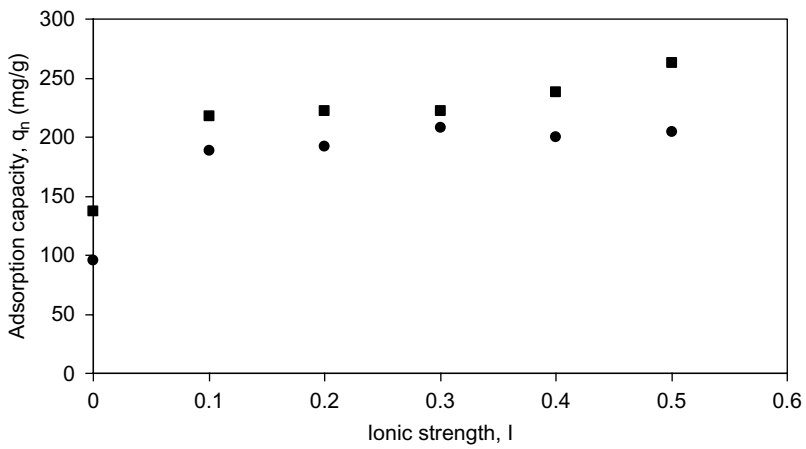


Figure 4. Influence of ionic strength on the adsorption capacity of UB saturated with Na^+ ions (●) and of SS saturated with Na^+ ions (■).

However, the adsorption capacities of the two samples towards AB 193 only increased slightly with increasing ionic strength. This is consistent with the results reported by Alkan *et al*. (2004). In their work, Alkan and co-workers increased the ionic strength up to 0.5 and showed that the adsorption capacities of clays were enhanced under these circumstances. This indicates that the positive charges on the surfaces of sepiolite and bentonite increase in number with increasing ionic strength, thereby yielding an increased adsorption capacity. Nevertheless, the maximum binding of anionic and cationic dyes at low and high pH values, respectively, was much less than the estimated number of charged groups, with the binding capacity varying with both the ionic strength and the dye concentration.

4. CONCLUSIONS

Acid dyes are water-soluble anionic dyes and are used to dye wool, nylon and silk fibres. Due to the weak interactions between the negatively charged surfaces of clays and anionic dyes, only a limited number of studies on the adsorption of Acid dyes have been undertaken using clay as an adsorbent. The adsorption of dyes in clay suspensions is greatly influenced by various features of the clay surface. The experimental results obtained in the present study may be summarized as follows.

1. The removal of Acid Blue 193 (AB 193) from aqueous solutions using sepiolite and bentonite as adsorbents has been investigated employing batch adsorption techniques. These adsorbents were shown to be effective and economical materials for the adsorption of AB 193 from aqueous solutions.
2. The values of the correlation coefficients obtained when the Langmuir adsorption model was applied to the experimental data indicated that this model provides the best description of the adsorption process. This supports the view that the outer surface of the adsorbent is covered by a monolayer of dye molecules during adsorption.
3. The amount of AB 193 anions adsorbed onto raw sepiolite was 1.44-times greater than that onto raw bentonite.
4. Cation saturation of the two adsorbents led to the replacement of a portion of the cations located at the edges of channels in the clay structure by Na^+ and Ca^{2+} ions. As a result, the reactivities of the surface groups located within the layers and at the edges of the clay structure were enhanced, with a consequent increase in the adsorption capacity of the saturated clay.
5. Both the pH value and ionic strength play an important role in determining the surface charge on the adsorbent and thereby influence the capacity of the adsorbent towards the adsorption of dye ions. It was found that the adsorption capacity of the two minerals towards AB 193 decreased with increasing pH but increased with increasing ionic strength.
6. When the adsorption capacities of the clay samples towards the cationic dye Methylene Blue (MB) (Bilgiç 2005) and the anionic dye Acid Blue 193 (AB 193) were compared, it was observed that cationic dye molecules exhibited a much higher affinity towards clay surfaces and were readily adsorbed when added to clay suspensions. This arises because the clay layers are negatively charged, leading to strong electrostatic attraction with cationic dyes. In contrast, large amounts of anionic dyes normally leak into wastewaters, leading to aquatic environmental contamination. The adsorption method developed in the present study has been shown to provide an efficient and economic process for removing the anionic AB 193 dye from aqueous solutions using natural adsorbents.
7. The adsorption of anionic dyes onto sepiolite and bentonite can be considered as a simple, fast and economic method for their removal from water and wastewater.

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