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Adsorption of Monovalent Cationic Dyes on Some Silicates

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Adsorption of two cationic dyes, methylene blue (MB) and malachite green (MG), was studied on the bentonite, sepiolite and zeolite samples by the batch equilibration technique using a spectrophotometer. In addition, cation exchange capacities (CEC) of samples were determined by NH_4^+ saturation using Kjeldhal distillation. The adsorption data was found to conform with the Langmuir equation within the concentration range studied, and Langmuir constants were determined for each of the samples. It was observed that the amount of dyes adsorbed was in excess of CEC in the case of bentonite and sepiolite. The adsorption capacities of the samples for both dyes have the following order: bentonite > sepiolite > zeolite.

Introduction

The adsorption of organic molecules on clay surfaces has been extensively studied[1]. Several studies have focused on the adsorption of cationic dyes to negatively charged smectites[2–5]. Adsorption of cationic dyes with clay minerals has been widely used as the basis for staining tests and identification[6]. Of the organocations, methylene blue has found considerable usage in the determination of cation-exchange capacity (CEC) and surface area of clays[7–9]. Margulies et al. suggested a method of photostabilization of pesticides based on coadsorbing on a clay surface the photolabile pesticide and adequate organic cation acting as energy acceptor[10,11]. The interactions between charged organic molecules and clays play an important role in determining the environmental behavior of certain organocations, some of which exhibit herbicidal properties. Many workers have shown that clay has the ability to reduce drastically the effects of herbicides[12]. Also, color removal from industrial effluents by adsorption techniques has been of growing importance. The chemical and biological stability of dyestuffs to conventional water treatment methods and the growing need for high quality treatment have made adsorption a very favorable treatment process. Equilibrium data, commonly known as adsorption isotherms, are the basic requirements for the design of adsorption systems.

It is well documented that organic cations adsorb to the clay surface significantly more strongly than inorganic cations, and that adsorption can proceed beyond the CEC of the clay[3,13]. A model was developed to evaluate the strength of the clay-organocation interactions[14].

The scope of this study is to determine the adsorption isotherms of two monovalent cationic dyes on some silicates with different crystal structures and to compare the CEC and adsorption capacities of the samples. Attempt have also been made to understand the adsorption mechanism in light of the structure of the dyes as well as of the clay minerals.

Experimental

Materials

The silicate samples used as adsorbents were two bentonite samples supplied from the ÇANKIRI and Ünye/ORDU regions, sepiolite from the Sivrihisar/ESKİŞEHİR and zeolitic tuff (which are rich in clinoptilolite mineral) from the Bigadiç/BALIKESİR region. The samples were named BT_1, BT_2, SP and ZT, respectively, and were dried at 105°C (24 h) and passed through a 200 mesh sieve. Chemical analysis of the bentonite samples was done at Eskişehir Cement Factory with an ARL 8680 XRF spectrometer, and results of chemical analysis of the sepiolite and zeolite samples were taken from the studies by Çetişli^{15} and İnel^{16}, respectively, and are given in Table 1. Differential thermal analysis (DTA) of the adsorbents done with Netzsch Geratebau 404 EP and DTA curves of the samples are given in Figure 1.

MB and MG (Figure 2) were obtained as chloride and oxalate salts, respectively, from Merck, and were used without further purifications.

Table 1. Chemical analysis of the samples

%	BT_1	BT_2	SP	ZT
SiO_2	33.41	37.17	56.906	72.16
Al_2O_3	9.77	7.80	0.085	11.84
Fe_2O_3	4.99	2.17	0.043	1.21
CaO	14.06	9.11	1.399	3.51
MgO	7.45	7.27	27.524	1.47
K_2O	3.09	0.13	0.013	1.86
TiO_2	-	-	0.008	0.09
Mn_2O_3	-	-	-	0.02
MnO_2	-	-	0.002	-
P_2O_5	0.31	0.03	-	0.01
Cr_2O_3	-	-	-	0.02
SO_3	0.03	-	-	-
Na_2O	1.16	6.15	0.019	-
LOI	19.22	15.08	14.0	-

Adsorption Isotherms

Portions of dye solutions (50ml) of known initial concentrations and varied amounts of adsorbents were poured into volumetric flasks. Analytical determinations of dyes in solutions after equilibration (48 hours at room temperature) were performed by means of a Shimadzu-120-01 spectrophotometer. Optical densities were determined at 663 nm and 617,5 nm, which correspond to the maximum absorption peaks of MB and MG, respectively, From the difference between initial and equilibrium concentrations, the amounts of dyes adsorbed were calculated. Errors due to dye adsorption on vessel walls were minimized by pre-aging all glassware with dye solution.

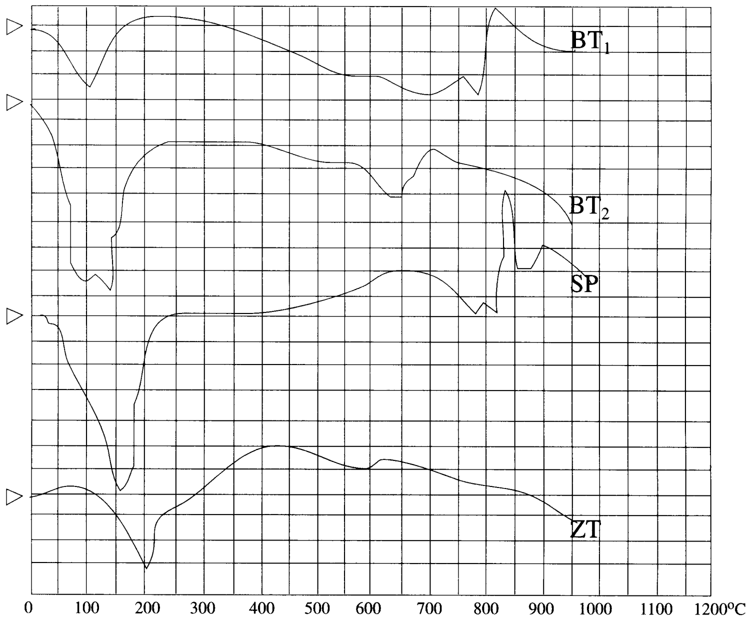
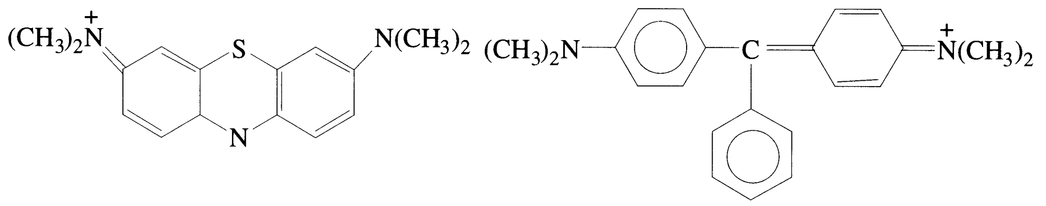


Figure 1. DTA curves of the samples



MB

MG

Figure 2. Structural formulae of the MB and MG

Cation exchange capacity

A mixture of the measured weight of sample and 1M ammonium acetate solution was shaken for 48 hours at 25° C to convert the sample completely to ammonium form. Then the sample was rinsed with distilled water and ethanol to remove excess ammonium. The NH_4^+-exchange sample was stirred with 0.1M HCl solution for 48 hours and the sample was completely converted to hydrogen form. Following filtration, the extent of exchange was determined by measuring the ammonium concentration in the solution. Ammonium was determined by steam distillation in the presence of a strong base (Kjeldhal distillation). The liberated NH_3 was collected in a 2% boric acid solution and titrated with H_2SO_4.

Results and Discussion

The adsorption data were analyzed according to the Langmuir equation[17,18].

$$\frac{Ce}{(x/m)} = \frac{1}{k \cdot b} + \frac{Ce}{b}$$

where Ce is the equilibration concentration of dye remaining in the solution, x/m is quantity of dye adsorbed per unit weight of adsorbent (surface excess). "b" and "k" are Langmuir constants. These constants are called adsorption capacity (maximum surface coverage) and bonding energy constant, respectively.

Straight lines were fitted to the points by the method of least squares, where the slope of the regression line is 1/b and the intercept is 1/kb. The linear regression lines obtained had highly significant correlation coefficients (r), indicating a good fit to the Langmuir equation.

The adsorption isotherms and Langmuir lines are shown in Figure 3-10. Langmuir constants and CEC values are given in Table 2.

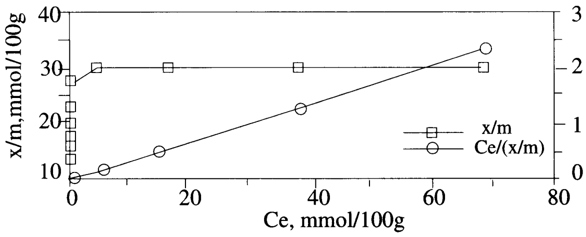


Figure 3. *BT*$_1$-MB adsorption isotherm and Langmuir line

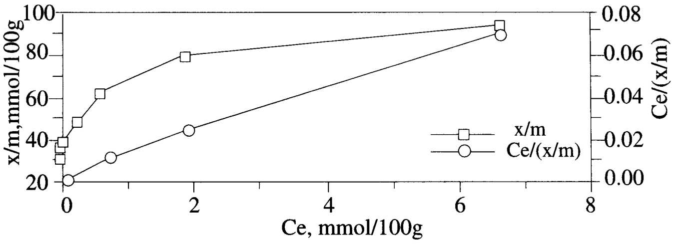


Figure 4. *BT*$_1$-MG adsorption isotherm and Langmuir line

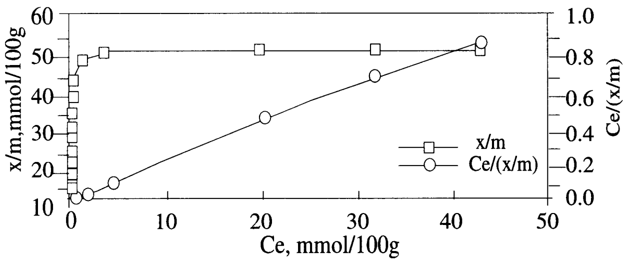


Figure 5. *BT*$_2$-MB adsorption isotherm and Langmuir line

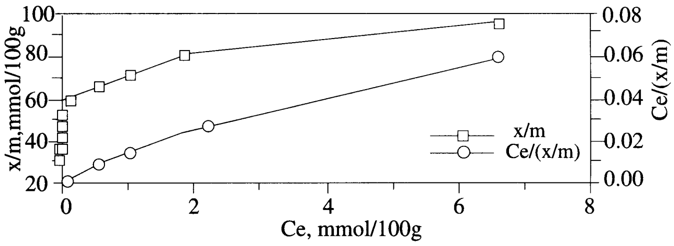


Figure 6. *BT*$_2$-MG adsorption isotherm and Langmuir line

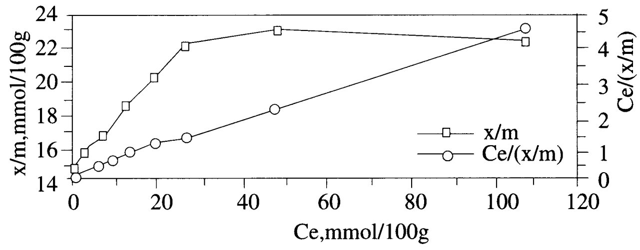


Figure 7. SP-MB adsorption isotherm and Langmuir line

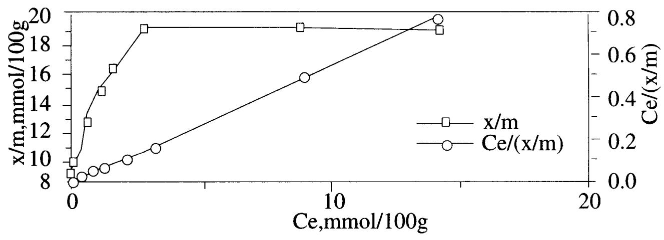


Figure 8. SP-MG adsorption isotherm and Langmuir line

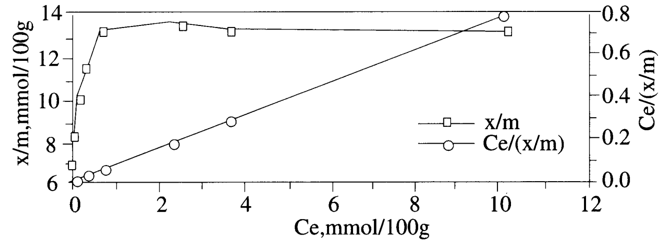


Figure 9. ZT-MB adsorption isotherm and Langmuir line

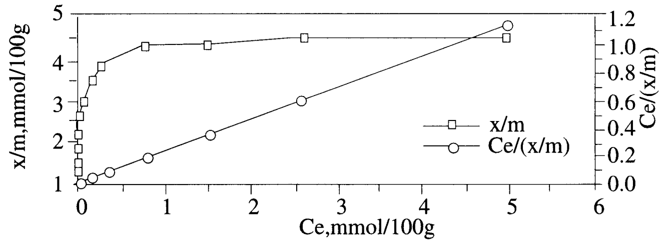


Figure 10. ZT-MG adsorption isotherm and Langmuir line

Table 2. Langmuir constants and CEC values

Silicates	BT_1		BT_2		SP		ZT	
Adsorbate	MB	MG	MB	MG	MB	MG	MB	MG
r(Corr.coeff.)	1.0000	0.9974	0.9999	0.9987	0.9992	0.9996	0.9999	0.9999
k(100 g/mmol)	-30.4545	5.8333	11.2941	12.6250	0.6238	5.2277	-763.0000	42.1321
b(mmol/100g)	29.8507	95.2381	52.0833	99.0099	22.6757	18.9394	13.1062	4.4783
CEC(meq/100g)	23.35		34.60		6.60		94.65	

The adsorption of certain dyes by clays from aqueous solutions was formerly considered to be physical only. It is now known that with cationic dyes at least, cation exchange first occurs, giving way to physical adsorption only when complete replacement of the original ions by basic dye ions has occured[9,19,20].

Small clay particles carry negative electrical charge, which can arise through a number of reasons. Probably the most important factor is substitutions within the lattice structure of trivalent aluminium (Al^{3+}) for quadrivalent silicon (Si^{4+}). Ions of lower valence may also substitute for Al^{3+} in the structure. These substitutions give rise to a deficiency of positive charge in the framework. This charge is balanced by mono and divalent cations elsewhere in the structure (exchangeable cations). In bentonites and zeolites it is concluded that about 90% of the total exchange capacity is a result of isomorphous substitution. Broken bonds around the edges of silica-alumina sheets on non-cleavage surfaces can give rise to unstatisfied charges, which need to be balanced by adsorbed cations. It is believed that this is a major reason for the low CEC of sepiolite, illite and chlorite minerals[6].

Giles et al.[21] found that monoionic dyes form monolayers of ionic micelles when adsorbed at a solid surface. The average number of dye ions per micelle depends only on the "ionic" weight of the dye.

Margulies et al.[14,22] employed an adsorption model that describes the adsorption of organic cations to negatively charged clays by means of two binding coefficients. This model is an extension of that described by Nir[23] in the sense that the monovalent organic cations can form charged complexes, in addition to neutral ones. In the following equation, X_i^+ denotes a monovalent cation that binds to single charged negative sites, P^-, on the surface of the clay. The reaction is:

$$P^- + X_i^+ \rightleftarrows PX_i \tag{1}$$

Organic monovalent cations can form charged complexes with the clay:

$$PX_i + X_i^+ \rightleftarrows P(X_i)_2^+ \tag{2}$$

The adsorption to montmorillonite of MB required a K_1 value (binding coefficient for reaction 1) of the order $10^8 M^{-1}$, whereas K_1 values for inorganic cations were at least six orders of magnitude smaller[14,23,24]. These data indicate that for amounts of added dye less than the CEC of the clay, practically all the added dye was taken up by the clay. However, when the amounts added were higher than the CEC, the amounts of Paraquate (divalent dye) adsorbed did not exceed the CEC, unlike the results for monovalent organic cations[22]. Adsorption of the organic cations at concentrations higher than the CEC of a clay should result in charge reversal of the clay. To verify this, a microelectrophoresis experiment was conducted[14].

In this study, dye adsorption capacities of samples for both dyes were found to decrease in the following order: bentonite > sepiolite > zeolite. Although the CEC of zeolite is much higher than those of bentonite and sepiolite, it has the lowest dye adsorption capacity. The crystal structures of zeolites are constituted of SiO_4 and AlO_4 tetrahedrals connected to each other via channels and pores. Exchangeable cations are found together with hydration water within channels in the framework. The system of channels and cavities is different in each zeolite structure, giving rise to a variety of materials, each capable of screening molecules and cations by molecular or ion sieving in slightly different manners[25]. Cation exchange takes place in the channels, but the dye cations are too large to pass through entry channels. It was therefore concluded that cationic dye adsorption by cation exchange mechanism is rather low for zeolite and the adsorption capacity of zeolite was found to be lower than those of bentonite and sepiolite. Compared to bentonite, sepiolite (fibrous structure) has lower CEC and lower adsorption capacity.

In this study MB and MG were found to be adsorbed in greater amounts than the CEC of bentonite and sepiolite. Also , MG adsorption capacity of bentonite samples was found higher than MB adsorption capacity.

De et al. found that the amount of dye adsorbed is in excess of CEC in the case of bentonite, whereas for the kaolinite, vermiculite, asbestos and feldspar, the adsorption is either equal to or less than the CEC[26]. In the literature, there are similar results for MB and crystal violet (CV) adsorption by clay minerals[7,27,28].

Narine and Guy[3] showed that the adsorption capacity of the K-and Ca- bentonite is $MG > MB$. Rytwo et al[29] found that crystal violet (CV) has a significantly greater capacity than MB to adsorb to bentonite. De et al.[26] found the adsorption capacities of H-bentonite for the cationic dyes to in the order $CV > MG > MB$. These data suggest that dye adsorption capacity of bentonite increases with the ionic weight of dye[30]. (Ionic weights of CV, MG and MB are 372, 330 and 285, respectively).

The adsorption of cationic dyes, although belived to be primarily an ion exchange process, is rather complicated by many factors other than the surface characteristics of the adsorbents, such as ionic size, molecular geometry[31], dye-dye interaction[19], inorganic "counterion" on the clay[3].

Conclusion

From the present work, the following conclusions were made;

1. The adsorption of monovalent cationic dyes on bentonite, sepiolite and zeolite was found to conform with the Langmuir equation.
2. Dye adsorption capacities of samples were found to decrease in the order bentonite >sepiolite > zeolite.
3. MB and MG have been found to be adsorbed in amounts greater than the CEC of bentonite and sepiolite.
4. MG adsorption capacity of bentonite samples was found higher than MB adsorption capacity.

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