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# Effect of pH Solution on the Optical Properties of Cationic Dyes in Dye/ Maghnia Montmorillonite Suspensions

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## Abstract

The interaction of three cationic dyes (Methylene blue, MB; Neutral red, NR; and Malachite green oxalates, MG) with montmorillonite clay from Maghnia deposit in aqueous suspensions was investigated using visible absorption spectroscopy. The stability of the optical properties of dyes in aqueous solutions and in dye/clay suspension was assessed in terms of the absorption bands maxima as a function of pH. The optimal pH for favorable adsorption of the dyes, i.e. ≥ 90% has been achieved in aqueous solutions at 6 for NR and at 7 for both MB and MG respectively. The adsorption of MB leads to the methacromatic effect. MB agglomerates occurred predominantly in the clay with high charge density, even with low charge density. The redistribution of MB molecules over the surface of clay at higher acidic medium causing a reduction of the dye aggregation. However, the interactions of NR and MG with clay differ in certain aspects from those of MB. The adsorption of NR is accompanied by a red shift of the main band at low pH, whereas, the conjugate form of NR, remains stable at neutral and higher pH. A blue shift of the main band is observed at pH 6, which is consistent with externally and internally adsorbed dye cations. For MG, a slight stability of the main bands in clay suspension at acidic and neutral pH, while, the band attributed to MG cations shifs to longer wavelengths at pH 9. To explain the relationship between the layer charge density and the adsorption, so- colled model 2-pKa of surface complexation (SCM) was developed.

**Keywords:** Clay; Adsorption; Dyes; Methachromasy; 2-pKamodel

## Introduction

Clay minerals, the most available, low cost and chemically active surface minerals world, are of great interest, practically because of their extensive uses in many scientific areas such as soil science (stoppage for fertilisers [1], photostabilizers of pesticides [2], industrial technology (heterogeneous catalysis [3], colloidal science (decontamination of water [4], pharmaceutical and paint industries [5] and photochemistry (guide for photo-redox reactions [6]. This clay is a dioctahedral smectite with isomorphic substitutions of $Al^{+3}$ by $Mg^{+2}$ with structural formula unit:

$$(Si_8)^{IV}(Al_{4-x}Mg_x)^{VI}O_{20}(OH)_4 \text{ where } x=0.5\text{-}0.9$$

However for Maghnia montmorillonite, part of the negative charge around 15-50% is due to tetrahedral substitutions of $Si^{+4}$ by $Al^{+3}$. This clay has an appreciable content of iron. The interest of clay minerals for wastewater treatment in recent decade owing to their catalytic properties and high capacity in the removal pollutants too stable and resistant for conventional methods such as the redox and the exchanging resins of ions [7], coagulation/flocculation [8], membrane separation [9], adsorption [10], the biological methods [11], and more recently the advanced processes of oxidation [12]. The adsorption of cationic dyes is performed via an ionic exchange mechanism. This means that the main dye-clay interaction is a coulomb-type interaction. However, other interaction, such as hydrophobic effect between guest molecules on the clay surface [13] and /or H-bonding [14] can contribute to the adsorption of organic dye on clay surface, favouring the dye agglomeration. Dye agglomeration was found to be sensitive to many parameters, such as the dye load, surface proprieties of the clay, exchangeable cations, the age of dye-clay suspension and pH solution [15].

It is commonly accepted that in clay-aqueous systems the potential of the layer surface charge is determined by the activity of ions (e.g. $H^+$ or pH). A convenient index of the tendency of a surface to become either positively or negatively charged as a function of pH is the value of the pH required to give zero net charge ($pH_{ZPC}$) [16]. $pH_{ZPC}$ is a critical value for determining quantitatively (sign and magnitude) the net charge (positive or negative) carried on the clay mineral surface during adsorption of reactive dyes.

In this work, the adsorption of three cationic dyes (Methylene blue, Neutral red and Malachite green oxalates) in aqueous solution with clay from a Maghnia deposit was investigated by the UV-Vis absorption spectroscopy. The effect of the optical properties of dyes in aqueous solutions and in dyes/ clay suspension was assessed in terms of the main absorption bands and the removal rate as a function of pH. To explain the relationship between the layer charge density and the adsorption, so-called Models of Surface Complexation (SCM) was developed using the 2-pKmodel.

## Materials and Methods

A thiazin group cation, Methylene blue (MB) (MW= 319.5 g.mol$^{-1}$, $\lambda_{max}$=665 nm, $\varepsilon$ =95000cm$^{-1}$ mole$^{-1}$dm$^3$), a phenazin group cation, Neutral red dye, NR (MW=288.8 g.mol$^{-1}$, $\lambda$ max=520 nm, $\varepsilon$ =25000 cm$^{-1}$ mole$^{-1}$dm$^3$) and triphenylemethane dye, Malachite green oxalate

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(MW= 507. 51 $g.mol^{-1}$, $\lambda_{max}$=617 nm, $\varepsilon$ =42000$cm^{-1}$ $mole^{-1}dm^3$) from Across product for microbiological analysis and was used as model dye without any further purification. Molecular structures of of dyes were shown in Figure 1.

Aqueous dye solution stock was prepared by dissolving accurately weighed neat dye in distilled water to the concentration of 1g/L. Experimental solutions were obtained by successive dilutions. Natural clay was supplied by the Ceramics Society of Maghnia (west of Algeria). The sodium form of clay with a particle size<0.2 µm was prepared in order to obtain good clay colloidal dispersions, as follows: clay was saturated with $Na^+$ by repeated exchange with NaCl (1M) aqueous solution. The <0.2 particle size fraction was separated by centrifugation and it was washed several times with distilled water until free $Cl^-$ was not detected in the suspension ($AgNO_3$ test). The <0.2 fraction was collected by centrifugation and freeze dried at 60°C for 24 h and is crushed. The Na-saturated clay material resulting from different treatments will be indicated by clay-Na.

X-ray fluorescence was performed on a spectrometer of mark (Oxford). The sample is powder tiny room and prepared (pearl borated) is subjected to a source of X-radiation of fluorescence characteristic of its chemical composition.

Adsorption experiments were carried out as a single-stage batch test using a magnetically stirrer. A suspension containing 0.03 g of adsorbent sample was mixed with a 100 ml aqueous solution of dye at a known initial concentration and initial pH in a flask at constant temperature of 298 K. The initial pH values of the solutions were previous adjusted with 0.1M HCl or NaOH using digital pH-meter (WTN: WISSENSCHAFLLICH TECHNISECHE WERKSTÄTTEN; weilehein Allemagne pH-330) pH-meter. Aliquot of the solution were withdrawn at a predetermined time intervals and were centrifuged (EBA-Hetlich) at 3500 rpm for 15 min to remove any adsorbent particles. Dye concentrations in the supernatant solutions were subsequently estimated by measuring absorbance at maximum wavelengths of dyes (UV – 2401 (PC) SHIMADZU – corporation spectrometer). The adsorption tests were continued until the equilibrium concentration was reached. The experiments were done by varying the initial pH from 3 to 13. The data obtained from the adsorption experiments were then used to calculate the removal rate of adsorbed dye A (%) Equation (1):

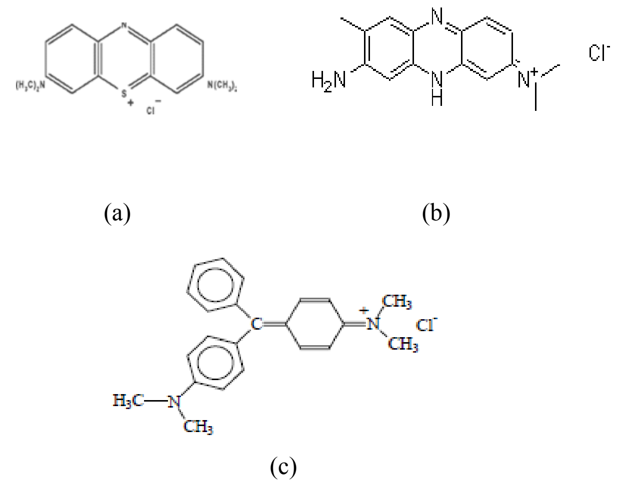

**Figure 1:** Molecular structures of dyes (a) Methylene blue (MB) (b) Neutral red (NR) and (c) Malachite green oxalates (MG).

| Element | Percentage by weight/unit / % |
|---|---|
| $SiO_2$ | 60.75 |
| $Al_2O_3$ | 24.15 |
| $Fe_2O_3$ | 2.51 |
| CaO | 1.56 |
| MgO | 2.54 |
| $Na_2O$ | 3.63 |
| $K_2O$ | 0.65 |
| $SiO_2/Al_2O_3$ | 2.52 |
| $SiO_2$+ $Al_2O_3$ | 84.90 |
| LIO | 5.21 |

LOI: Loss on ignition

**Table1**: XRF analysis of the clay-Na sample.

$$A(\%) = (\frac{C_0 - C_e}{C_0})100 \qquad (1)$$

where $C_o$ and $C_e$ are the initial and equilibrium solution concentrations (mg/L) respectively.

## Results and Discussion

### XRF analysis of the clay-Na

Table 1 displays the results of chemical composition in the Na-clay sample. The major elements of the clay-Na, expressed in terms of oxide, are primarily of silica, and alumina with appreciable iron content. The CaO and $Na_2O$ ($K_2O$) reflect the contents of interlayer cationic in clay. The other oxides present in traces amounts such. In the perfect montmorillonite structure, the total theoretical content of $SiO_2$ and $Al_2O_3$ is 92% [**17**] and the content ratio of $SiO_2$ to $Al_2O_3$ is 2.6. In the Maghnia clay, the total content of $SiO_2$ and $Al_2O_3$ is 84.90% and the corresponding ratio of $SiO_2$ to $Al_2O_3$ is 2.52, so this type of clay belongs to the Na-montmorillonite category. The cation capacity of exchange and total specific surface of the clay-Na sample were estimated by the methylene blue (MB) method [18] are of 101.72 meq /100gr of clay-Na and 673.93 $m^2$/g respectively.

### Qualitative study: The evolution of maxima absorption bands of dyes in aqueous solution and in dyes/clay- Na suspensions at various pH.

Figure 2 illustrates the evolution of absorption bands maxima of dyes in aqueous solution and adsorbed onto clay-Na at various pH values. The location of the absorption bans maxima of dyes are collected in Table 2.

The visible spectra of MB in aqueous solution show that MB exhibits a main band at 668 nm assigned to the absorption of monomers and associated with a shoulder attributed to the 0-1 vibronic transition of monomers $MB^+$ at about 605 nm. The MB monomers have nearly constant absorption bands and absorbance intensities over the pH values in the range of pH between 3 and 13, while the shoulder is most sensitive to the pH solution. The absorbance of the vibronic shoulder at about 605 nm increases and shifts slightly to 624, 621 and 610 nm at pH 7, 11 and 13 respectively, whereas no change is observed in 605 nm-shoulder at pH 3, 5 and 9 respectively. The increase and the bathochromic shift in 605 nm-shoulder are attributed to the partially self-association of MB monomers as cationic dimmers in face-to-face arrangement to minimize their hydrophobic interaction with water [19].

In contrast, Neutral red, in solution at various pH values, exhibits two forms: NR$^+$H and NR, which are in equilibrium with each other. NR, which has absorption bands in the range of 451-454 nm under neutral and alkali conditions (pH≥ 6), whereas NR$^+$H, is found to lie between 518 and 521.5 nm under acidic media (pH<6). On the other hand, for MG, the pH has no effect on the absorption bands (at around 617 nm is attributed to the absorption of monomer cations, MG$^+$ and near 425 nm is assigned to the protonated cations, MG$^{2+}$H) of MG dye, thus affirming their high stability over the pH range of 3-9. At high alkaline medium (pH>9) the colorless carbinol base is formed. Such an effect was observed for the similar malachite green [20], methyl green [21], and crystal violet [22].

The behavior of the bands maxima of MB adsorbed onto clay-Na with the pH is characterized by a hyposochromic shift of the main absorption of MB$^+$ with respect to those in aqueous solutions. The maxima appear at 585, 588, 584, 567 and 566 nm at pH 5, 7, 9, 11 and 13 respectively. The shifts exceed 50 nm, which is consistent with that observed with MB [23]. In the most case, this change consists of a substitution of the main absorption bands, which correspond to the absorption of monomers, MB$^+$, by new absorption bands placed at shorter wavelengths, the so-called methachromatic effect. The methachromasy observed in several clay/dye systems been attributed to different processes:

(i) An intermolecular interaction between the electronic π-system of the dye with the electron lone-pairs of the oxygen atoms at the clay surface,

(ii) The self-association of dye molecules when they are adsorbed on the clay surface.

The π- interaction is proposed for clays with partial tetrahedral substitution of Si$^{+4}$ by Al$^{+3}$. Since Clay-Na has this type of substitution, methachromatic effect has to be related to the π- interaction [24]. Such profile was reported for the analogous Methylene blue [25].

However, the main band of MB$^+$ at pH 3, gradually shifts from 648 nm (in aqueous solution) to longer wavelengths, almost reaching 658 nm (in clay-Na suspension) and the relative intensity of vibronic shoulder (around 605 nm) increases. The observed shift can be attributed to the change in the environmental polarity/acidity of negatively-charged clay surface with respect to water surrounding, suggesting that the adsorption process is instantaneous. Shift to higher wavelengths of ≈ 10 nm are always observed for dye monomers adsorbed at the clay surface.

As seen in Figure 2, the interactions of NR and MG with clay-Na differ in certain aspects from those of MB. The adsorption of NR$^+$H is accompanied by a slight red shift of the main absorption bands to longer wavelengths under pH range of 3-5, whereas the NR (conjugate base) form has a nearly constant absorption bands over the pH range of 8-12. At pH 6, the band maximum shifts from 518 nm (in aqueous solution) to shorter wavelengths, almost reaching 460 nm (in clay-Na suspension). These results are consistent with externally and internally adsorbed monomer cations (pH<6), monomer cation-conjugate base equilibrium at pH=6 and shifting the monomer cation-conjugate base equilibrium to the conjugate base form (pH>6) respectively.

On the other hand, for MG, the results (given in Table 2) show a slight stability of the main bands of both forms (MG$^+$ and MG$^{2+}$H) in clay-Na suspension under pH values in the range of 3–7, while, the absorption band attributed to MG$^+$ shifted to longer wavelengths at pH 9, almost reaching 631 nm with respect to that in aqueous solution.

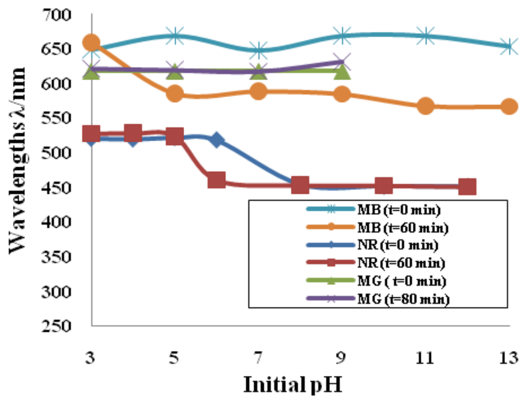

**Figure 2:** Evolution the main absorption bands of dyes in aqueous solution and in dyes/clay-Na suspensions as a function of pH for [MB]= [NR]= [MG]=50mg/L, [Clay-Na]=0.3g/L, T=298K and contact time=60 min (MB and NR) and 80min (MG).

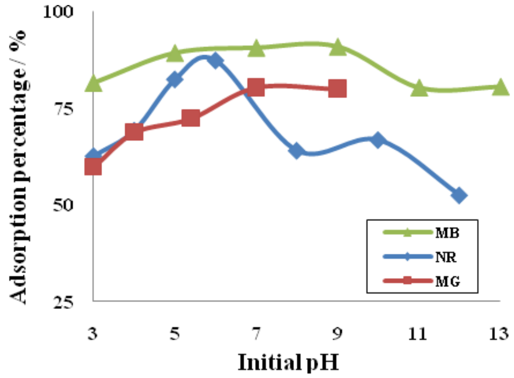

**Figure 3:** Effect of the pH on the absorption bands maxima of MB in aqueous solution and in dyes/ clay-Na suspensions for [MB]= [NR]= [MG]=50mg/L, [Clay-Na]=0.3 g/L, T=298K and contact time of 60 min (MB and NR) and 80min (MG).

The shift did not exceed 10 nm over the pH range of 3- 5 and 3-7 for NR and MG respectively, but is significantly higher for NR at pH 6 and MG at pH 9, being 14 and 58 nm respectively. Such an effect was observed for the similar Malachite green [26].

Shift to higher wavelengths of ≈10 nm are always observed for dye monomers adsorbed at the clay surface. The observed shift can be attributed to the change in the environmental polarity/acidity of negatively-charged clay surface with respect to water surrounding, suggesting that the adsorption process is instantaneous [27].

In addition, this change is accompanied by the appearance of new band at 596 nm placed in shorter wavelengths assigned to an influence on π-orbital. Such influence might be caused by an adjacent platelet, indication flocculation or by the formation of dimers on the surface of the clay-Na [28].

## Quantitative study: The evolution adsorption rate of dyes in dyes/clay-Na suspensions at various pH.

The effects of initial pH solution on the adsorption rate of BM and NR onto clay-Na were investigated over a range of pH values from of 3 to 13, while for GM; the experiments were conducted over a range

| MB /aqueous solution | | | MB⁺/clay-Na | | NR /aqueous solution | | NR /clay-Na | | MG/aqueous solution | | MG/ clay-Na | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| pH | $MB^+$ | $(MB^+)_2$ | $MB^+$ | $(MB^+)_n$ | $NR^+H$ | NR | $NR^+H$ | NR | $MG^+$ | $MG^{2+}H$ | $MG^+$ | $MG^{2+}H$ |
| 3 | 648 | - | 658 | *608 | 520.5 | - | 527 | - | 617 | 424 | 621 | 426 |
| 4 | - | - | - | - | 519.5 | - | 527.5 | - | - | - | - | - |
| 5/ 5.4 | 668 | 624 | - | 585 | 521.5 | - | 523.5 | - | 617 | 425 | 619 | - |
| 6.5/ 7 | 647 | - | - | 588 | 518 | - | - | 460 | 617 | 424 | 617 | 426 |
| 8/ 9 | 668 | - | - | 584 | - | 454 | - | 452.5 | 617 | 423 | 631 / 596 | - |
| 10 | | - | - | - | - | 451.5 | - | 452 | Col. | Col. | Col. | Col. |
| 11 | 668 | 621 | | 567 | - | | - | | Col. | Col. | Col. | Col. |
| 12 | - | - | - | - | - | 451 | - | 450.5 | Col. | Col. | Col. | Col. |
| 13 | 653 | 610 | - | 566 | - | | - | | Col. | Col. | Col. | Col. |

$MB^+$, $(MB^+)_2$ and $(MB^+)_n$ : monomer, dimer and agglomerates forms of Methylene blue dye.
$NR^+H$ and NR: monomer and conjugate base form of Neutral red dye. Col.: colorless.
$MG^+$ and $MG^{2+}H$: monomer and protonated cations forms of Malachite green oxalate dye.

**Table 2**: Evolution the main absorption bands of dyes in aqueous solution and in dyes/clay-Na suspensions as a function of pH for [MB]= [NR]= [MG]=50mg/L, [Clay-Na]=0.3g/L, T=298K and contact time=60 min (MB and NR) and 80min (MG).

of pH values from 3 to 10 for avoiding dye degradation. As shown in Figure 3 & Table 2, the pH significantly affected the adsorption percentage of all the three dyes. The dye adsorption rate increased from 81.47% to 90. 81% for MB and from 62.52% to 87.19% for NR as the pH was increased from 3 to 7 for MB and from 3 to 6.5 for NR respectively, and then decreases to 80. 46 and 52.39 % at pH =13 and 12 for MB and NR respectively. However, for MG, the adsorption raised from 59.84 to 80.40% when the pH value was increased from 3 to 7 then it remains constant beyond pH=7. The maxima adsorptions of dyes of 90.81, 87.19 and 80.40 % for MB, NR and MG were achieved at pH 7, 6 and 7 respectively.

The adsorption of these charged dye (thiazin, MB; phenazin, NR; and triphenylemethane, MG ) groups onto the adsorbent surface is primarily influenced by the surface charge of the adsorbent, which is in turn influenced by the solution. For clay minerals the potential determining ions are $H^+$ and $OH^-$ and complex ions formed by bonding with $H^+$ and $OH^-$. The broken Si–O bonds and Al–OH bonds along the surfaces of the clay crystals result in hydrolysis, is an amphoteric surface hydroxyl group that can associate (Equation 2) and dissociate (Equation 3) proton.

To explain the relationship between the layer charge density and the adsorption, so-called the Surface Complexation Model of (SCM) was developed [29]. In the 2-pKa approach we assume two reactions for surface protonation.

At low pH the reaction might be:

$$\text{Si-OH} + H^+ \leftrightarrow \text{Si-OH}_2^+ \qquad (2)$$

Lower adsorption rate of dyes at low pH is probably due to the presence of excess $H^+$ ions competing with the cations groups on the dyes for the adsorption sites.

However, the high removal rate observed for NR at pH 6 (low pH) is attributed to the formation of surface hydrogen bonds between the surface of the hydrogen bonds of the hydroxyl group on the clay-Na surface and the nitrogen atoms of neutral red cations [30]. At high pH the reaction is:

$$\text{Si-OH} + OH^- \leftrightarrow \text{Si-O}^- + H_2O \qquad (3)$$

In our studies the adsorption maximum for both MB and MG dyes are achieved at pH 7 respectively. So at neutral and high pH, the solution in contact with the basal oxygen surface of the tetrahedral sheet will contain excess hydroxyls. The surface will then exhibits a cation exchange capacity (Equation.4):

$$\text{Si-O}^- + \text{Dye}^+ \leftrightarrow (\text{Si-O}^-, D^+) \ (4)$$

The adsorption rate of MB dye decreases with increase in pH (above pH 9), then becomes constant up to pH 13. Such decrease is assigned to the presence of dimers $(MB^+)_2$ species in the clay-Na environment competing with the monomers $(MB^+)$ on the dyes for the active sites.

On the other hand, at neutral and higher pH (>10), most NR dye occurs in the form of undissociated molecules. Indeed, the presence of the neutral form of NR molecules in the clay-Na atmosphere increases the local concentration favoring the aggregation followed by precipitation of the dye.

## Conclusion

The effect of the optical properties of dyes (MB, NR and MG) in aqueous solutions and adsorbed onto Maghnia clay was assessed in terms of the absorption bands maxima and the adsorption rate as a function of pH solutions. The adsorption of MB dye onto clay surface leads to the methacromatic effect in the absorption spectrum of the dye. Formation of MB dimers and higher agglomerates reflected sensitively the potential of the layer surface charge density. MB agglomerates occurred mainly in the clay with high charge density, even at low charge density.

The adsorption of NR onto clay-Na is accompanied by a red shift of the main absorption at low pH, whereas, that of NR, has a constant absorption bands at high pH. A blue shift of the main band is observed at pH 6, consistent with externally and internally adsorbed monomer cations and shifting the monomer cation-conjugate base equilibrium to the conjugate base form respectively.

For MG, a slight stability of the main bands in clay-Na suspension at acidic and neutral pH, while, the band attributed to $MG^+$ shifs to longer wavelengths at pH 9, almost reaching 631 nm. The observed shift can be attributed to the change in the environmental polarity/acidity of negatively-charged clay surface with respect to water surrounding, suggesting that the adsorption process is instantaneous.

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The optimal pH for favorable adsorption of the dyes, i.e. ≥ 90% has been achieved in aqueous solutions at 6 for Neutral red and at 7 for both Methylene blue and Malachite green respectively. The relationship between the layer charge density and the adsorption is explained by the 2-pKa surface complexation model (SCM).

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