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SORPTIVE INTERACTION STUDIES OF MALACHITE GREEN ON CATIONIC SURFACTANT MODIFIED CLAY

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ABSTRACT

Clay minerals are ubiquitous in natural systems and several studies have been carried out to establish the remediation potential of this geochemical on organic pollutants. In this study, the natural clay was modified using cationic surfactant; quaternary ammonium salts, hexadecylpyridiniumchloride (HDPy) and hexadecyltrimethylammonium bromide (HDTMA), producing three sets of sorbents including the native clay sample. The main objective of this research is to study the adsorption behaviour of malachite green dyes onto the surfactant modified natural clays. The results of Scanning electron microscopy (SEM) and Fourier Transform infrared (FTIR) confirmed the intercalation of organic moiety into the clay. The adsorption results showed that the dyes were in a good agreement with Langmuir isotherm in both types of modified clays. The value of separation factor, K_L, from Langmuir equation and Freundlich constant, n, gave an indication of favourable adsorption. The maximum adsorption capacity, qm, based on Langmuir model was 181.5 – 281.5 mg/g at 25 °C and is in agreement with the experimental values for practical applications.

Keywords: Adsorption, Clay, Freundlich model, Langmuir model, Surfactant.

INTRODUCTION

The study of mechanisms of sorption of chemicals has been a veritable tool for effectively predicting the mobility, transport, speciation and possible remediation of the chemicals in the environment. Malachite green dye (MG) may have detrimental impact on human health and the environment in general and it has been used extensively as model dyes for adsorption studies onto various low cost adsorbents [1]. MG is largely utilized as food additives such as colouring agent, and a therapeutic disinfectant as well as a dye in many industries [2]. There are reports that MG causes carcinogenesis, mutagenesis, chromosomal fractures, teratogenecity, respiratory toxicity and multi-organ tissue injury [3]. Irrespective of the facts, malachite green dye still find application in aquaculture and other industries. In the past, much research has been focused on the development of adsorbents from natural sources. For example, naturally occurring clays, zeolites, and other cheap and readily available solid materials are used to remove dyes from wastewater [4]. Beside the vast applications of dyes, dyes have now turned into an exceedingly questionable compound because of the risks they pose to consumers, including its effects on the immune and reproductive system [5, 6].

Clay minerals are appropriate for adsorption process based on some of its physico-chemical properties, which include specific surface area and nanometer-scale size [7]. Adsorption of dyes on activated carbon has been proven to be effective in removing dyes from aqueous solutions. However, activated carbon is still considered expensive and currently research is focused on the development of low-cost adsorbents for this purpose. A number of non-conventional sorbents such as sugarcane dust, algae, sawdust, bottom ash, fly ash, de-oiled soya, maize cob, peat, iron humate, mixed sorbents, microbial biomass, activated slag, waste product from agriculture, magnetic nanoparticle and coal have been tested for malachite green dye adsorption [8-13]. Recent progress in the synthesis of nanostructured materials offers a broader spectrum to change surface properties of naturally occurring clays in order to increase their adsorption properties

The aim of this study was to examine and compare the adsorption capability of natural clay (montmorillonite) and surfactant modified clay for removal of malachite green as a model dye from aqueous solutions. The clay was amended with a cationic surfactant, Hexadecyltrimethylammonium bromide and Hexadecylpyridinium chloride, in order to assess the changes in the clays and its adsorption capacity. The structures of natural and organoclay were assessed by utilizing FT-IR spectroscopy, and SEM. The impacts of various parameters: pH, contact time, dye concentration and adsorbent dosage were also studied. The adsorption systems of dyes (MG) onto clay were assessed in terms of adsorption isotherms which were portrayed by utilizing Langmuir and Freundlich isotherm models.

MATERIALS AND METHODS

Materials

Both quaternary ammonium salts, hexadecylpyridiniumchloride and hexadecyltrimethylammonium bromide were purchased from Sigma- Aldrich and used without any purification. The cationic dyes malachite green (MG) $C_{23}H_{25}C_lN_2$ (96%) were used as the adsorbate in this study and obtained from Sigma-Aldrich (Germany). All the chemicals used were of analytical reagents grade.

Clay modification

The surfactant modified clays were synthesized using the general procedure described below. The clay impurities were removed by sedimentation method, followed by oven drying at 110 °C for 3h and pulverized through 200 µm sieve. Briefly, 30 mL of the quaternary ammonium

Salt solution (1:1 CEC) was placed in a beaker and 1g of pre-dried clay was added into it. The mixture was stirred with the magnetic stirrers for about 16 h at room temperature, followed by centrifugation and washing several times with deionized water until no halides ions were detected from the supernatant. The modified clays were oven dried at 60 °C for 5 h, ground to 74 µm sizes, and finally stored in a desiccator for use [14].

Characterization

The physicochemical characteristics of the adsorbent materials are important in evaluating the mechanism of sorption onto the surface of the adsorbent. The chemical analysis of the natural clay and modified clay was determined using X-ray fluorescence (XRF) spectrometer (Phillips PW 1404 Xray). The FT-IR spectra of natural and modified clay were recorded to examine the surface functional group using Nicolet Nexus 870 FT-IR spectrometer in the region 500–4000 cm^{-1} with resolution of 4 cm^{-1} and ten interferograms was recorded for each sample. An FEI Quanta 450 scanning electron microscope (SEM) was used to define the change in surface morphology of natural and modified sorbent. The surface area was determined using Sear's method and cation exchange capacity (CEC) of the clay was measured using a simple $BaCl_2$ method [15].

Adsorption Studies

The sorption study of dyes on modified clay was carried out by batch equilibrium experiment of known amount of the adsorbent with 50 mL of aqueous dye solutions of known concentration in a series of 100 mL stopper flasks. The solution mixtures were kept under isothermal conditions in a shaking water bath at 150 rpm at the desired temperature. At predefined time based on kinetic reports on malachite green, the solution mixtures were removed from the shaker, and centrifuged. The residual dye concentration in the reaction mixture was analyzed by UV/Vis spectrophotometer (Shimadzu UV1700 Japan) using calibration curve. The effect of various experimental factors, namely, pH, adsorbent dose, initial dye concentration and contact time were investigated employing the univariate approach. After each adsorption experiment, the suspensions were centrifuged, filtered through 0.45 μm of nitrocellulose membrane (Sartorius Stedim Biotech. GmbH), to remove the solid organoclays particles and the supernatant were subsequently analysed by spectrophotometer for the residual concentration of the MG. The amount of each solute adsorbed (Cs, mg/g) was calculated as follows:

$$Sorption\ Efficiency\ (S\%) = \frac{(C_o - C_e)}{C_o} \times 100$$

$$q_e = \frac{(C_o - C_e) \times V}{m} \qquad (1)$$

Where C_o (mg/L) is the initial concentration, C_e (mg/L) is the equilibrium solute concentration, V_o is the initial volume and S_m is the mass (g) of the soil [14-17]

Data Analysis

Two model of isotherm where used to fit the sorption data. The Freundlich model (FM), which is used commonly for quantifying dye sorption equilibria for soils, has the following form;

$$Q_e = K_f C^N_e \qquad (2)$$

where Q_e is the solid-phase concentration (µg/g) and C_e is the liquid-phase equilibrium concentration (µg/L). K_f is the sorption capacity-related parameter (µg/g)/(µg/L)^n) and n is the isotherm nonlinearity index, an indicator of site energy heterogeneity [18] determined by linear regression of log-transformed data as shown below:

$$\log Q_e = \log K_f + N\log C_e \qquad (3)$$

The Langmuir model (LM) describing such site-limiting sorption equilibrium has the following form

$$Langmuir: q_e = \frac{q_m K_L Ce}{1 + K_L Ce} \qquad (4)$$

where q_{max} is the maximal sorption capacity and K_L is a solute–surface interaction energy-related parameter [19].

RESULTS AND DISCUSSION

Material Characterization

Physico-chemical Characterization

Table 1: Sorbent Characterization

SORBENTS	PH	TOC(%)	DOC	S/A(m^2/g)	PZC	CEC	K_{FOC}
UNTREATED CLAY (MMt)	6.3	4.6	5.82	56	6.5	68.3	0.098
HDPy-Clay	5.7	5.2	6.67	14.5	7.0	66.55	0.107
HDTMA-Clay	6.2	7.3	7.25	16.5	7.3	59.28	0.145

The clay utilized was a montmorillonite (MMt) (Smectite clay) found in Adekunle Ajasin University campus. There are many MMt deposits available in Nigeria. The data on the physic-chemical characterization of sorbents is presented in Table 1. The native clay and the modified clay have a close pH and organic carbon content. Chemical compositions of MMt was ((total weight %) 57.38} 0.11% SiO_2, 2.33} 0.05% MgO, 15.20} 0.10% Al_2O_3, 1.10} 0.03% K_2O, 4.07} 0.06% CaO, 2.72} 0.03% Na_2O, 0.1} 0.02% SO_3, 6.49} 0.07% (FeO + Fe_2O_3) as determined by XRF. Results of XRF showed that predominant exchangeable cation was calcium along with sodium and potassium. The cation exchange capacity (CEC) of MMt clay was 68.3meq/100g and surface area of 56m^2/g for natural clay. The pH_{ZPC} of the treated and untreated sample (MMt) is 6.5 for natural clay and 7.0, 7.3 for HDTMA and HDPY-clay respectively. The determination of pH_{ZPC} (i.e. the pH at which the mineral's surface charge becomes zero) is of great importance for clay, as its major mineral constituent encompass hydroxyl ions into their structure. The latter are very reactive, contributing to the net mineral electric charge. At pH < pH_{ZPC} raw clay exhibits a net positive charge, whereas at pH > pH_{ZPC} a net negative charge (20, 21).

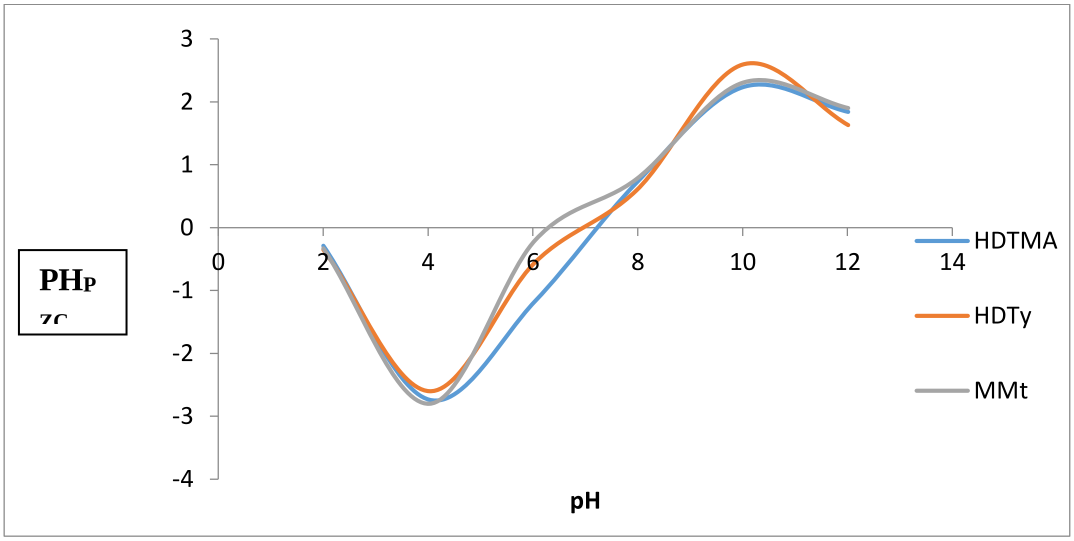


Figure 1: Plot of Point Zero Charge (pH_{PZC}) of natural and treated clay

Fourier Transformed Infrared Spectrocopy

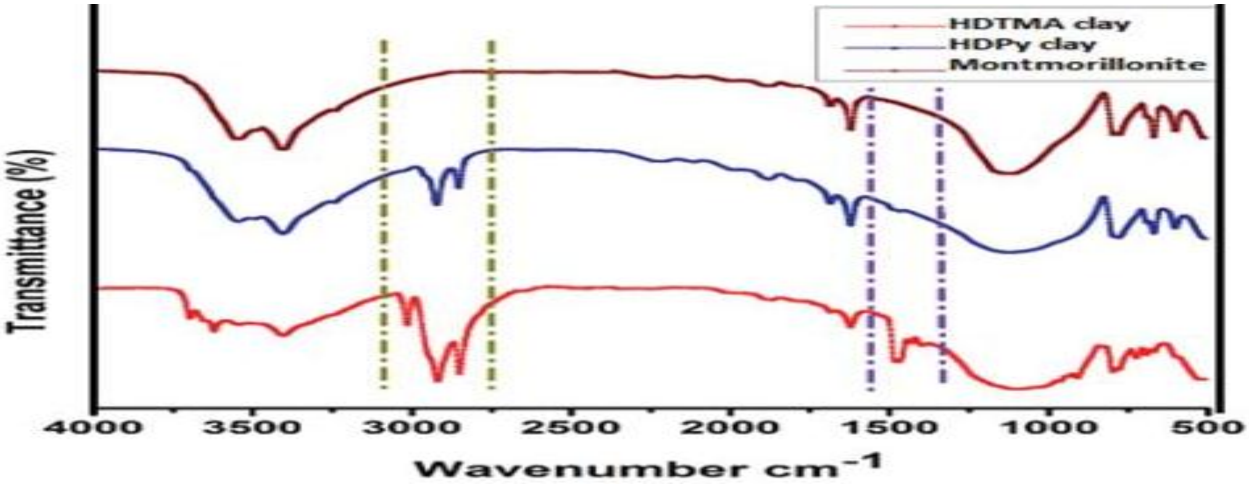
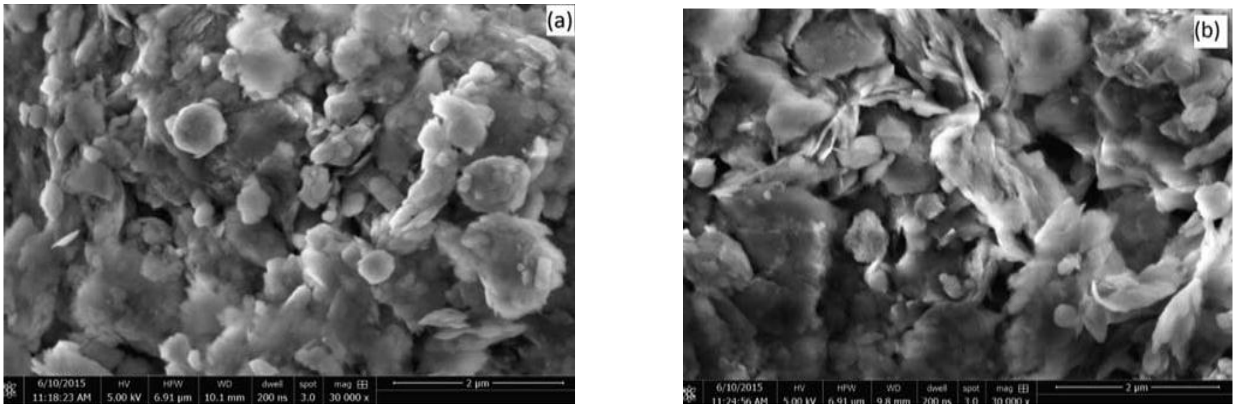


Figure 2: FT-IR spectral for the Sorbents

To comprehend the presence of functional groups onto the surfaces of the adsorbent with and without modification, the FT-IR spectral analysis was performed within the range of 400–4000 cm^{-1}. The FT-IR spectra of natural clay, HDP-clay and HDTMA-clay are shown in Figure 1. The IR region between 3700–3000 cm^{-1} shows the region of OH stretching and is observed by two key bands, which is also observed in almost all the natural hydrous silicate (Fig. 1). Different stretching vibrations of OH are present in this region. A peak at 3621 cm^{-1} for MMt is assigned to OH stretching vibrations for the structural hydroxyl group attached to the octahedral magnesium and the tetrahedral silicon. The bands at 3404 and 3243 cm^{-1} can be ascribed to water molecules, within the layers of the clay which are hydrogen bonded adsorbed. The bands between 3500–3000 cm^{-1} are relatively dependent on the concentration of surfactant loaded on clay and become broad upon loading. The conformational changes of the surfactant loading on clay can be monitored through the sensitive CH stretching bands. The CH stretching region (2700 and 2900 cm^{-1}) for the clay loaded with surfactant molecule shows asymmetric vas(CH$_2$) and symmetric vs (CH$_2$) stretching modes of 2920 cm^{-1} and 2853cm^{-1}. The region between 1700–1600 cm^{-1} shows the HOH bending of adsorbed water molecules in both clay and organoclays (Fig.1. peak observed at 1641 cm^{-1}). The strong band between 1100–900 cm^{-1} for natural clay and organoclays were assign to the Si–O–Si and Si–O–Al stretching. The peak between 920–810 cm^{-1} agrees with OH deformation linked to the Mg and Al. The peaks between 800–620 were corresponds to the Si–O quartz vibrations [14].

Scanning Electron Microscopy



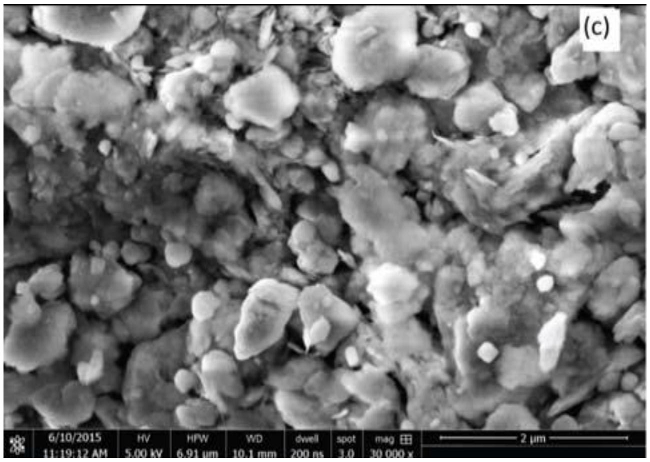


Figure 3: SEM images of sorbents (a) Natural Clay (MMt) (b) HDTMA-Clay (c) HDPy-Clay

The SEM micrographs of natural clay and Surfactant modified clays are shown in Figure 2. Small particle size, smooth and micro-porous surface with fluffy appearance due to the closely packed flakes were observed. The surface area of unmodified MMt clay was 56 m^2/g, whereas the modified MMt clay shows the decrease of surface area to 16.5 m^2/g and 14.5 m^2/g for HDTMA and HDPy surfactant respectively. These results are attributed to the fact that most of the exchange sites of MMt clay are occupied by organic surfactants molecules with large molecular size and the inaccessibility of the internal surface to nitrogen gas [22]. However, larger average pore size (10.2 nm) was observed in modified clay than the precursor clay (3.2 nm). After the modification of clay with HDMA and HDPy surfactant, the surface morphology slightly changed from foliated structure to non-agglomerated and crumpled structure containing heterogeneous pores with large particles as depicted in Figure 2. MMt have massive and curved plates (Fig. 2) generally as a heterogeneous surface morphology [18]. However, the clay modified with organic surfactants shows significant changes in the morphology. Compared with the morphology of the MMt, there are many small and aggregated particles and the plates become relatively flat in while the introduction of organic moiety lead to large particles and coarse porous surface, which may be due to the penetration of organic molecules into the galleries of MMt, resulting in an increase in the adsorption capacity of modified clay [4].

Adsorption studies

Effect of Initial Concentration

The initial concentration of adsorbate (dyes) plays important role in adsorption capacity of organoclays [23, 24]. The influence of initial dye concentrations was examined using 0.02 g of the HDPy and HDTMA-clays at pH 7 with equilibrium time of 60 min. Figures 4 and 5 show that adsorption of dyes onto modified clays increases with increase in the concentration of dyes in a solution up to a certain value after which it leveled off. This is because of the fact that an increase in the concentration of dye solution produces high mass gradient pressure between the dye solution and sorbent. This pressure gradient acts as a driving force for the transfer of dye molecules into the particle surface of the clays {1, 15, 25].

Table 2: FM and LM sorption parameters for sorption of Malachite Green to treated and unmodified Clay (pH 7.0).

Sorption Model		**MMt**	**HDPy-clay**	**HDTMA-clay**
FM	K_f	75.7	99.6	128.4
	n	4.43	6.64	5.54
	R^2	0.9969	0.9738	0.9786
LAGM	q_{max}	181.5	265.2	281.5
	K_L	0.037	0.148	0.27
	R^2	0.9582	0.9876	0.9885

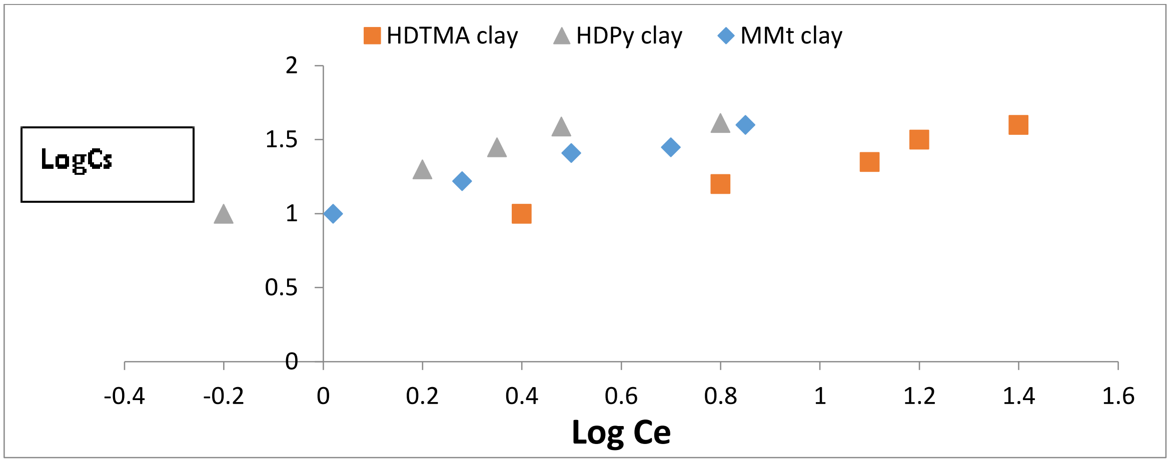


Figure 4: Plot of Freundlich isotherm for the Modified and Unmodified Clay.

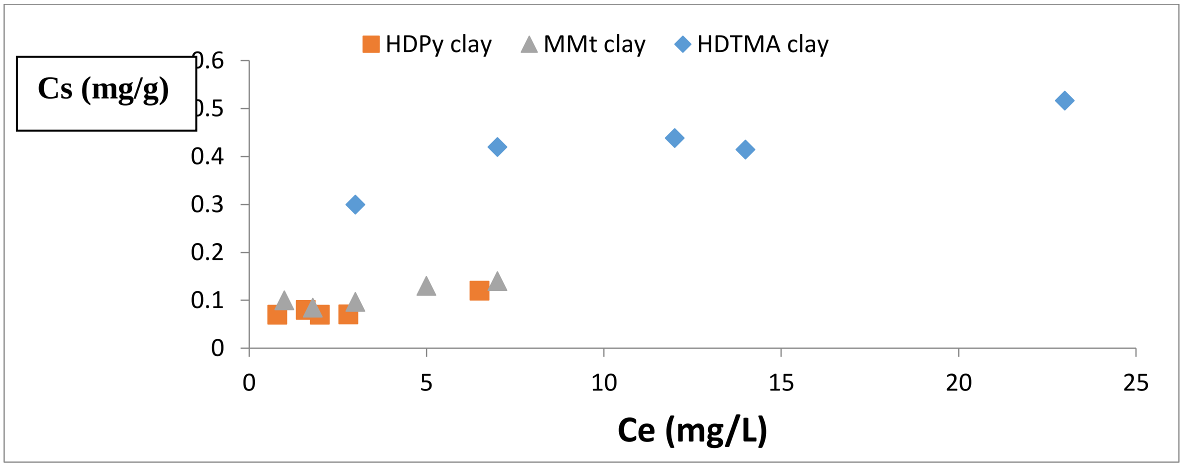


Figure 5: Plot of Langmuir isotherm model for the modified and Unmodified Clay

This non linear solute-sorbent interaction has been previously reported. Georgiadis et al. [21] stated that certain factors that could influence the mechanisms of adsorption are the aggregation of the suspended particles [26, 27], the occupied volume of the suspended particles [28], the solute transfer rate onto the surface of the adsorbent [29] and the potential splitting of the amount of dye compounds adsorbed onto the unit weight of the adsorbent [24]. The optimum experimental value for solid to solution ratio for geomedia would be a value representative of the natural conditions. However, the values obtainable in natural conditions are too high to be used in batch experiments (e.g. in solids the ratio tends to unity) [30].

For malachite green dye concentrations of 20 mg/L ≤ Co ≤ 100 mg/L, solid to solution ratio equal to 1:100 g/ml, solution pH = 5.3 ± 0.2, surfactant-modified alumina as adsorbent and at ambient temperature, the optimum time for malachite green removal was 30 min [31]. The adsorption capacity K_f for the untreated and treated clay ranged from 75.7-128.4 g/g and correlation coefficient, $R^2 \geq 0.95$. The adsorption of capacity of the surfactant modified clay showed higher adsorption capacity. However the HDTMA shows the highest values compared with the three sorbents.

The adsorption of malachite green onto surfactant-modified clay fits into the Langmuir model isotherm, with qmax ≥ 281 mg/g for initial adsorbent quantity of 0.02 g for HTDMA soil, showing the highest adsorption capacity. Similar values were obtained from studies carried out using other non-conventional adsorbents, such as neem sawdust, sugar cane dust, hen feathers and arundo donax root carbon [8, 9, 13, 31, 32].

The results also indicate that percent removal and adsorption capacity of dye onto the clay shows opposite trends by varying the concentration of dye solution. Several researchers also found the same adsorption results as function of MG dye concentration [19, 32, 33]. The inverse patterns for the adsorption capacity and percent removal can be clarified with the way that: there are fixed number of binding sites on the clay surface. At the point when the dyes are available in little concentration, the adsorption will be fast and the percent removal of dyes will be high because of the higher number of accessible sites on the surface of clays. The quantity of accessible sites for adsorption is higher at lower dyes concentration and deceased with the increase in the concentration of dyes because of the saturation of adsorbed dye molecule. The dye molecules at high concentration compete with each other for the fixed number of binding sites. Thus, some of the dye molecules did not get adsorbed and remained in solution, causing lower percent removal of dyes [14, 34].

Effect of Initial pH

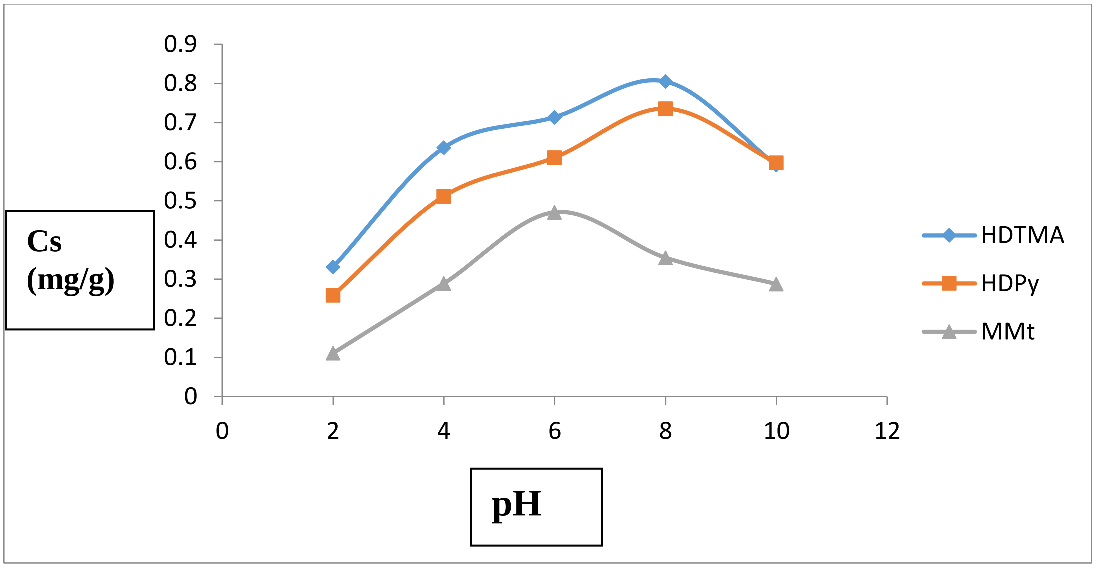


Figure 6: Plot of Concentrations Vs pH

To investigate the role of pH on the sorption capacity of HDTMA- and HDPy-organoclays for the MG, adsorption experiments were carried out with an initial dye concentration of 100 mg/L and mass of sorbents was 0.1g. The vials were equilibrated for a period of 30 min at varying initial pH, ranging from 2–10. Figure 6 reveals that with increasing pH of a solution, the adsorption of cationic dyes also increases. Fundamentally, cationic dyes produces molecular cations (C^+) and reduced ions (CH^+) on dissolution in water and depends on the water pH. At lower pH, the surface of the adsorbent become protonated which resulted in lower adsorption of the protonated dyes [35]. Increase in adsorption of dyes with the increase of pH from 2 to 12 was because of the way the overall positive charge in aqueous solution diminished. At neutral pH, it showed a balanced surface charge that was required for the adsorption [25, 36, 37].

It was observed that dye adsorption showed little increase in sorption after pH 7 and considering the value of pH_{pzc} of the sorbents, a decline in adsorption of the dye is justified as there will be electrostatic repulsion as pH of solutions tends to basic region.

CONCLUSION

The performance of hexadecyltrimethylammonium/Hexadecylpyridinium-intercalated montmorillonite clay for the removal of malachite green from aqueous solutions has been investigated in this study. The surface and physical properties of clay and surfactant modified clay were evaluated using SEM, FTIR and other standard analytical methods. The results indicated the successful intercalation of these surfactants onto clay. The experimental data were fitted to the Langmuir and Freundlich isotherm equations. The results indicate that the experimental data fit well for both the isotherm models. However, the regression coefficient (R^2) values of Langmuir isotherm for dyes are better than that of the Freundlich isotherm, which indicate that adsorption of dyes takes place via a monolayer mechanism on the surface of the modified clay. Further the experimental maximum adsorption capacity is well matched with the qm calculated from the Langmuir isotherm model.

The results and unique findings of the study can be used to successfully predict the mechanism of adsorption of other cationic dyes and possible treatment or remediation strategies that can be adopted for dye or textile waste water.

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