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RESEARCH ARTICLE

ADSORPTION CAPACITY OF TILEMSI PHOSPHATE ROCK ON BASIC DYE IN AQUEOUS SOLUTION: METHYLENE BLUE CASE

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ABSTRACT

Valorization of the Malian phosphate rock as an adsorbent requires the determination of its performances in terms of kinetics and maximum adsorption capacity. The potential of Tilemsi Phosphate Rocks (TPR), to remove methylene blue (MB) from aqueous solution was evaluated in a batch. Experiments were carried out as function of contact time, initial concentration (25–200 mg/L), pH (4–12) and temperature (20-60˚C). Adsorption isotherms were modeled with the Langmuir and Freundlich isotherms. The data fitted well with the Freundlich isotherm. The experimental data were analyzed by using two kinetic models: the pseudo first order, pseudo second order models. The results shows that equilibrium is quick, and the data were best described by the pseudo second-order model (R^2= 0.99). The amount of the dye adsorbed increases with the mass of adsorbent. The adsorption process dependent pH with a high adsorption capacity at pH =4. The dye adsorption equilibrium was attained after 40 min of contact time. Removal of dye in acidic solutions was better than in basic solutions. The adsorption of (MB) increased with increasing initial dye concentration. The equilibrium data were revealed that Langmuir model was more suitable to describe the (MB) adsorption. Thermodynamic study showed that the adsorption was a spontaneous and endothermic. The results indicated that the Tilemsi phosphate rock could be an alternative for more costly adsorbents used for dye removal.The TRPcould be useful in implementation of a new cheap technology for textile wastewater treatment.

INTRODUCTION

Artisanal dyeing provides employment to thousands of Malian women [1]. The synthetic dyes used by these women often come without any labels. The wastewater generated contains various types (acids, basic, dispersive...) of dyes. It also contains heavy metals such as chromium, copper, lead, and zinc, the content of which exceeds 0.1 mg/l4. This wastewater is often discharged directly, without any preliminary treatment, into the environment [2]. Many of the synthetic dyes contain complex chemical structure that makes them stable (hence, not easily biodegradable) and persist in the environment [3, 4]. Methylene blue (*MB*) is the most used substance for dying cotton, wood, and silk. It can cause eye burns which may be responsible for permanent injury to the eyes of human and animals. On inhalation, it can give rise to short periods of rapid or difficult breathing while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, profuse sweating, mental confusion and methemoglobinemia [5–7].

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The removal of color from wastewater becomes a challenging the textile industry consumes a lot of water and generates an important quantity of effluents highly charged with pollutants, which constitute a serious threat for the environment. In recent years, the removal of the contaminants from wastewater has been extensively studied using various physicochemical and biological techniques [4,5,6]. Although various treatment methods, such as coagulation precipitation[7], electroflotation [8], membrane separation [11], oxidation [10] and adsorption processes [9-12] can be used to reduce the quantity of toxic substances present in textile wastewater. Among of these processes, adsorption is one of the most effective methods and this process has aroused considerable interest during recent years. Activated carbons are very efficient and have been preferentially used for the adsorption of dyes [13]but their use is restricted due to high cost. Therefore, there is growing interest in using alternative adsorbents that are cheaper and commercially available. Taking in to account their availability and its low cost, Tilemsi Phosphate rock *(TPR*) Constitutes a possible alternative of adsorbent that could be used for the removal of dyes from textile wastewater and, more generally, in industrial wastewater. Numerous studies have shown that phosphate minerals, both natural and active, have the potential to adsorb heavy metal ions from aqueous solutions [14-15].

However, to our knowledge, few studies have been published on the removal of textile dyes by natural phosphates [16-17]. In our case, we are interested in removing dyes from wastewater by Tilemsi Phosphate Rock *(TPR)*, a very abundant material in Mali. In this context, the naturel phosphate rock was characterized and evaluated for the adsorption of Methylene Blue *(MB)* dye. The pH, mass of adsorbent, temperature, concentration dye and contact time were studied.

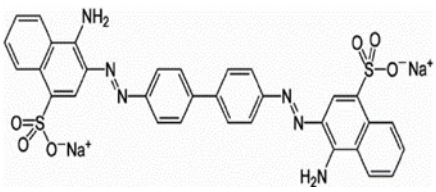
MATERIALS AND METHODS

Materials

Adsorbent: The adsorbent used in this study is natural phosphate. Tilemsi Phosphate Rock ***(TPR)*** deposits are localized in the valley of Tilemsi next to In-Tassit in the north of Mali. The staff of the Toguna (agro Industry) provided the sample. It is in the form of a beige powder. The powder was washed with distilled water to remove the impurities dried in an oven at 105°C for 48hours. In order to obtain good homogeneity of powder, the sample obtained is ground and then sieved. The choice of this material is based on its low cost, considering its abundance in Mali

Adsorbate: The Methylene blue dye was obtained from a Laboratory of University of Minnesota (Campus Crookston) as a commercially available dye formulation and was used without further purification. The solutions were prepared by dissolving the required amount of dye in distilled water. The concentration of the dyes was determined, respectively, using a UV spectrophotometer ("UV-2005", Selecta, USA), at the maximum wavelength (λ_{max}) of 664 nm. The structure and characteristics of Methylene blue dye are illustrated below.

Methylene Blue (MB):



chemical structure

Name: **3,7-Bis(dimethylamino)phenothiazin-5-ium chloride. Molecular Formula: $C_{16}H_{18}N_3Cl$.**

Molecular Weight:319,86g/mol

Methods: Adsorption experiments were performed by the batch technique to obtain rate and equilibrium data. Batch adsorption experiments were carried out to investigate the effect of initial dye concentration, contact time, pH, and temperature on the adsorption of methylene blue on Tilemsi phosphate rock. The experiments were carried out in 150 ml conical flasks by mixing a pre-weighed amount of adsorbent with 50ml of methylene blue dye solution. The adsorbent dosages were checked from 0.5 – 2g/L. The mixture was stirred at constant speed (500 rpm) for few minutes. After, the solid was separated from the mother solution by filtration through a sintered glass and the dye concentration was determined using the UV–vis spectrophotometer. The isotherm study was carried out at different temperature from 10 to 60°C with the initial dye concentrations of 10 to 50mg/l. The kinetic study was done by varying time from 1 to 60minutes. The effect of pH was observed by studying the adsorption of dye over a pH range of 2 – 12. The pH of the dye solution was adjusted with 0.1N HCl or 0.1N NaOH solution by using a pH- meter (EUTECH Instrument, pH 510). The equilibrium adsorption capacity was calculated using the following equation,

$$\text{Concentration of dye: } C = \frac{(C0-Ct)}{m} * V \quad (1)$$

Where C_0 and C_t are the liquid phase concentrations of dye at the initial and equilibrium conditions, respectively, V is the volume of solution (L) and m is the mass of adsorbent used (g).

The percentage of dye removal was calculated from the relationship:

$$\%\text{ of dye} = \frac{(C0-Ct)}{C0} * 100 \quad (2)$$

where C_0 is the initial dye concentration and C_t (mg/L) is the concentration of dye at equilibrium.

RESULTS AND DISCUSSION

Characterization of the Adsorbent : The Analysis by (FT-IR) spectroscopy of Tilemsi phosphate rocks shows a fluor-apatite carbonate type B [18 19]. It highlights several bands, those attributable to phosphate ions. We find the same bands relating to phosphate ions in the spectrum of tricalcium phosphate ($Ca_3(PO_4)_2$). The position, intensity and identification of the bands are listed in table1. The infrared spectrum not showing the characteristic bands of hydroxyl ions (3560cm^{-1}) makes it possible to affirm that one is in the presence of fluorapatite [20, 21].Some of the crystal-chemical characteristics of TPR have been determined previously, It is a carbonate apatite. Apatite is a group of phosphate minerals. It contains 23 to 32% of P_2O_5 and its solubility [22] in neutral ammonium citrate is 4.2%. It has a unit-cell a-value of 9.331 as determined by X-ray diffraction studies [23]. The specific surface area of Tilemsi PR is reported to be 26.4 m^2/g.

Mineralogical Analysis of Phosphate Rocks

Table 1. Position and identification of bands observed in IR

Position(cm^{-1}) and band intensity	identification of bands
564,08(strong) - 601,23(strong)	phosphate ions
865,32(low)	carbonate apatite
1928(very strong) – 1093(average)	phosphate ions
1429(low)	carbonate apatite

Parameter study

•**Effect of solution pH:** The pH of dye solution plays an important role in the whole adsorption process, particularly on adsorption capacity [24]. The influence of the pH of the solution on the adsorption was studied using different pH values: 2, 4, 7, 9 and 12. The experiments were carried out by adding 2g of natural phosphate to 50 ml of the dye solution (100 mg • L^{-1}) at constant temperature 24°C. The pH of the colored water-phosphate system was adjusted to the desired values by adding HCl (0.1N) to acidify or NaOH (0.1N) to basify.

Table 2. Chemical composition analyzed by x-ray fluorescence of phosphate rocks of Tilemsi.

Compound	CaO	P_2O_5	SiO_2	F	Al_2O_3	SO_3	Na_2O	MgO	Fe_2O_3	K_2O
%C	42.5	31.5	7.29	6.98	2.83	2.54	0.955	0.651	0.328	0.093
Element	O	Ca	P	F	Si	C	Al	Na	S	Mg
% C	43.1	30.6	14.3	5.98	2.94	2.73	0.97	0.708	0.618	0.393

The Table 3 presented the results of the analyzes on the effect of pH on dyes adsorption. The effect of pH on the adsorption of MB at equilibrium (q_e) by *TRP* show that: the qe was found to increase with increasing pH. Lower adsorption at acid pH was probably due to the presence of excess of H^+ ions competing with the dye cations for adsorption sites. At higher pH values (7–12) the dye adsorption was almost constant. The surface of *PRT* may contain a large number of active sites, and the solute (dye) uptake can be related to the active sites and also to the chemistry of the solute in the solution. At higher pH, the surface of *PRT* particles may become negatively charged, which enhances the positively charged MB cations through electrostatic forces of attraction [24].

Table 3. The results of the analyzes on the effect of pH on MB dye adsorption

pH	2	4	7	9	12
qe	1.639	1.758	1.665	1.664	1,664
%R	98.37	99.05	98.78	98.71	98.71

Effect of initial dye concentration: The amount of adsorption for dye removal is highly dependent on the initial dye concentration. The effect of initial dye concentration depends on the immediate relation between the concentration of the dye and the available sites on an adsorbent surface. In general, the percentage of dye removal decreases with an increase in the initial dye concentration, which may be due to the saturation of adsorption sites on the adsorbent surface. On the other hand, the increase in initial dye concentration will cause an increase in the capacity of the adsorbent and this may be due to the high driving force for mass transfer at a high initial dye concentration [25]. In this study 2g of natural phosphate was added to 100 mL of each of the solutions of every dye, the initial concentration of which was (4, 8, 12, 16, and 20 mg / L^{-1}. Time =10, 20, 30, 60, 90mn; temperature= 24°C). Effects of initial dye concentration and contact time shows the adsorption uptake versus the adsorption time at various initial *MB* concentrations. The amount of dye adsorbed ($q_e$mg/g) increased with increase in time and then reached equilibrium. The amount of dye removed at equilibrium increased from 4,175 to 19,316 mg/g with the increase in dye concentration from 4 to 20 mg/L. We notice that the amount of dye adsorption increased with increase initial dye concentration. The removal of dye depends on the concentration of the dye. Table 4. presented the results analyzes on the effect of initial dye concentration on adsorption.

Effect of temperature: Effect of temperature is another significant physico-chemical process parameter because temperature will change the adsorption capacity of the adsorbent [26]. If the amount of adsorption increases with increasing temperature, then the adsorption is an endothermic process. This may be due to increasing mobility of the dye molecules and an increase in the number of active sites for the adsorption with increasing temperature. Whereas the decrease of adsorption capacity with increasing temperature indicates that, the adsorption is an exothermic process. This may be due to increasing temperature decreasing the adsorptive forces between the dye species and the active sites on the adsorbent surface because of decreasing the amount of adsorption [27].The effect of temperature on the adsorption rate of Methylene Blue on *PRT* was investigated at 20, 30, 45and 60 ˚C. Increasing the temperature is known 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 temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate [28]. The adsorption capacity increased from 23,674 to 25,58 mg/g when temperature of the solution was increased from 20 to 60 ˚C, indicating the process to be endothermic (Table 5). This may be a result of increase in the mobility of the dye with increasing temperature. An increasing number of molecules may also acquire sufficient energy to undergo an interaction with active sites at the surface. Furthermore, increasing temperature may produce a swelling effect within the internal structure of the TRP enabling large dye to penetrate further.

Effect of amount of adsorbent: Adsorbent dosage is an important process parameter to determine the capacity of an adsorbent for a given amount of the adsorbent at the operating conditions. Generally, the percentage of dye removal increases with increasing adsorbent dosage, where the quantity of sorption sites at the surface of adsorbent will increase by increasing the amount of the adsorbent. The effect of adsorbent dosage gives an idea for the ability of a dye adsorption to be adsorbed with the smallest amount of adsorbent, to recognize the capability of a dye from an economical point of view [29]. The study of the effect of the mass of rock phosphate on the adsorption of the dyes was be carried out as follows: Concentration of the dyes: 100 mg/L, pH =4, Temperature: 24°C, Time of contact: 60 min;Mass of phosphate rock: 0,15g to 2g. The Table 6. shows the analyzes result on the effect of adsorbent dosage on the percentage of dye removal by Tilemsi rock phosphate. We represented the change in the percentage removal of the dye depending on the mass of used phosphate rocks. for 1.5 g of phosphate rock of Tilemsi (PRT), can eliminate 98.45 % of Methylene Blue.

Effect of time contact: Contact time was one of the effective factors in adsorption process. The percentage of Methylene Blue adsorption was studied as a function of contact time in the range of 5-60 minutes. The results obtained were presented in Table 7. It was observed that with the increase of contact time, the percentage adsorptions also increased. Minimum adsorption was 95,80 % for time 5 minutes to maximum adsorption value 98.30 % for the time 60 minutes for 50mg/L initial concentration of dye solution. The adsorption characteristic indicated a rapid uptake of the dye. The adsorption rate however decreased to a constant value with increase in contact time because of all available sites was covered and no active site available for binding,

Adsorption isotherm: Adsorption Isotherms or equilibrium data are helpful to describe the sorption interaction and adsorption capacity of adsorbent.

Table 4. Effect of initial concentration on adsorption of the Methylene Blue

t min	Initial Concentration C_0 (mg/l)				
	4 mg/l	8 mg/l	12 mg/l	16 mg/l	20 mg/l
	adsorbed Quantities (mg/g)				
10	3,416	7,416	10,735	13,837	17,757
20	3,491	7,416	10,742	13,887	18,043
30	3,595	7,543	11,786	15,217	18,445
60	3,657	7,638	11,346	15,066	18,876
90	4,175	7,670	11,356	15,167	19,316
120	4,333	8,057	11,994	15,184	18,750

Table 5. The effect of temperature on the adsorption rate of of Methylene Blue

T(°C)	20	30	45	60
R(%)	92,42	93,84	94,24	98,30
Qt	23,674	24,485	24,509	25,58

Table 6. The effect of the mass of rock phosphate on the adsorption of the Methylene Blue

m_{PRT}(g)	0,15	0,30	0,60	0,80	1	1,5	2
Ct (mg/L)	0,857	0,940	0,987	1,366	1,508	2,159	2,230
R(%)	95,70	95,80	97,10	97,40	98,20	98,45	98,30

Table 7. Effect of Time contact on the adsorption of Methylene Blue

t (min)	5	10	20	30	60
R (%)	95,80	97,10	97,40	98,20	98,30
Ct (mg/L)	0,840	0,887	1,266	1,408	2,059
qt (mg/g)	24,58	24,56	24,36	24,29	23,97

Table 8. Isotherm parameters for removal of MB at different temperatures

Isotherms	Parameters	Temperatures (K)		
		303	313	323
Langmuir	Q_o (mg/g)	82.64	123.45	142.86
	b (L/mg)	0.085	0.044	0.05
	R^2	0.98	0.93	0.97
Freundlich	Kf(mg/g $(L/mg)^{1/n}$)	7.88	6.297	6.79
	n	1.57	1.326	1.24
	R^2	0.99	0.99	0.99

For the purpose of the study of Isotherm Methylene blue on the surface of Tilemsi phosphate rock, different concentrations of the dye mentioned above were obtained, with 20 ml of each concentration added to 1,5 g of surface and placed in a water bath vibrating for 30 minutes at 24 ° C, After the adsorption period was finished, the absorption of the samples was measured at the maximum wavelength of the dipstick, and then the amount of adsorption was calculated. and the equilibrium concentration (Ce) and determine the adsorption isotherms dye on PRT carbon by plotting a graph between extent of adsorption (log q) and equilibrium concentration log Ce[30] , The relationship between log q and log Ce is called Freundlich adsorption isotherm. The logarithmic equation for Freundlich adsorption isotherm is given by following expression;

$$\text{logqe} = \text{logKf}+(\frac{1}{n})Ce$$

Where Kf and 1/n are Freundlich constants related to adsorption capacity (L/mg) and adsorption intensity respectively. A plot of log qe versus log Ce was used to calculate the value of Kf and 1/n from intercept and slope respectively. These values are given in table 8. , The chemical equation for Langmuir adsorption isotherm is given by following expression.

$$C_e/q_e=1/Q_0b+C_0/q_0$$

Where: Ce is the equilibrium concentration of dye (mg/L); qe is the amount of dye adsorbed at equilibrium (mg/g); Q0 (mg/g) and b (L/mg) are the Langmuir constants. The plot of Ce/qe versus Ce gives straight line (R2=0.98). The slope and intercept of the plot were used to calculate the values of Q^o (mg/g) and b respectively, which are given in table 8. K_f and n values can be calculated from the slope of the straight line. The Freundlich parameters and the results are represented in table 8. A value for n ranging between 0 and 1 is a measure of surface heterogeneity, becoming more heterogeneous as its gets value closer to zero [32]. The n values are between 0 and 1 representing beneficial adsorption. A value of n less than one indicates that better adsorption mechanism and formation of relatively stronger bond between dye molecules and adsorbents. This shows that Tilemsi phosphate Rock are better adsorbent for the methylene blue. Values of K_f for removal of dye by Tilemsi phosphate Rock indicates that adsorption capacity of the adsorbent. The higher the K_f values greater is the adsorption capacity of an adsorbent. Results shows that the experimental data was better described by the Freundlich isotherm model compared to the Langmuir isotherm model. The value of correlation co-efficient (R^2) is regarded as a measure of the goodness-of- fit of experimental data.

The values of correlation co-efficient (R^2) indicated that the adsorption process conforms to the Freundlich isotherm model. This shows that the experimental data was better explained by the Freundlich isotherm model (R^2 = 0.933 to 0.960) compared to the Langmuir isotherm model. This indicates that the adsorption of methylene dye on Tilemsi phosphate Rock takes place as monolayer adsorption on the adsorbent surface, homogenous in adsorption affinity.

CONCLUSION

The Natural Phosphate of Tilemsi, an inexpensive and easily available material, was found to very effective to remove MB from aqueous solutions. The equilibrium data were analyzed using the Langmuir and Freundlich isotherm models. The maximum monolayer adsorption capacity was found to be 91.90 mg/g at 24^0C. Equilibrium data fitted very well with Freundlich isotherm equation. The kinetics of the adsorption process was found to follow the pseudo-second-order kinetic model. This study reveals that Tilemsi phosphate material can be used as an environmental reactant in wastewater treatment. The TPR adsorption is mainly attributed to hydrogen bonding and electrostatic interaction between dyes species and oxygen-containing functional groups on the carbon surfaces.

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