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Development of geopolymers based on local clay for the depollution of industrial wastewater

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Abstract

During this study, geopolymers were developed from natural clays, collected in the village of Etigbo in southern Benin. The objective of this research is to evaluate the adsorption potential of modified clay with respect to methylene blue. Several kaolinite-based geopolymers were prepared with different ratios of SiO_2 */*Al_2O_3 *and an alkaline activator. X-ray diffraction (XRD) analysis of the samples showed amorphous structure favorable for the adsorption of dyes. Adsorption tests were carried out using the geopolymer named Eti24 and different parameters (contact duration, pH effect of pH, initial concentration of the dye, etc.) have been studied to optimize the MB process of removal. Studies of the adsorption kinetics of this dye on the geopolymer were also carried out. The adsorption equilibrium showed that the absorption kinetic is of pseudo-second order and more compatible with Freundlich model. The results revealed that the Eti24 geopolymer can serve as a basis for more sophisticated methods of treating aqueous effluents.*

Keywords: Geopolymer, kaolinite, adsorption kinetics, methylene blue.

Introduction

The population boom and increasing urbanization, combined with the industrial developments of our century, have led to the deterioration of water, air and soil quality. With the rapid development of industries, water pollution is becoming of particular concern. Increasing the bioavailability of water via the removal of dyes from wastewater is a current topic of great interest.

Indeed, dyes are commonly used in a variety of industries, like plastic, paper, textile and leather manufacturing[1]. Discharging effluents that contain dyes into water without prior appropriate treatment poses risks to the environment and public health[2]. Methylene blue (MB), water-soluble cationic dye, and one of the most widely used textile dyes in the industry[3,4] can have negative effects on living creatures such as breathing difficulties, diarrhea, vomiting, nausea and other harmful impacts on aquatic environment[5,6]. Therefore, it is necessary to reduce its concentration in wastewater.

Many techniques are available for degrading pollutants in wastewater: biological treatments: biological treatments[7], biochemical methods[8], membrane separation[9], ion exchange[10], electrochemical processes[11], coagulation/ flocculation[12], adsorption[13], etc. Adsorption has certain advantages over the different methods cited above in terms of ease of use, efficiency and low cost. This method has therefore attracted more and more interest and many scientists have been interested in the synthesis of new adsorbents with higher pollutant fixing power[14-18].

Many studies have highlighted the effectiveness of the activated carbon[19-23], one of the most versatile adsorbents. However, it is not widely used because it is difficult to regenerate and expensive[24-26]. This is why continued attention is paid to clays, taking into account their abundance in nature and the importance of their exchange surfaces[27,28].

Inorganic geopolymers have been the focus of research efforts for the optimization of clay adsorption capacity[29,30] .

In this vein, we evaluated the possibility of modifying natural clays collected in *Etigbo* (Southern Benin) into geopolymers with a view to their use as adsorbents for industrial dyes.

Material and Methods

Materials: In this study, aluminosilicate materials, CTAB and sodium hydroxide were used for the development of geopolymers. The clay ore which is kaolinite was also used. The commune of Kétou, located in the Plateau department of Benin, was the place where this ore came from, precisely in Etigbo and in a well 11m deep according to the following geographical coordinates: in the North: 07°20'12,7"; to the East: 002°33'54.4". An aqueous solution of sodium hydroxide was mixed with sodium silicate for the development of geopolymer materials. Studies carried out on several materials have shown that the aqueous solution of sodium hydroxide (NaOH) produces better dissolution of the aluminosilicate than that of potassium hydroxide[31].

Other materials were used such as: agathe mortar, 10% hydrochloric acid solution, multiparameter, digital flocculator 10408, oven (Prolab).Methylene blue or tetramethylthionine hydrochloride with the chemical formula $C_{16}H_{18}ClN_3S$, was chosen for the adsorption tests as a model organic dye because of its widespread use in laboratories. It is available, toxic and used as a dye for dyeing cotton, silk and wood.

For the adsorption tests, methylene blue, with the chemical formula $C_{16}H_{18}ClN_3S$, was chosen as a model organic dye, because of its wide use in the laboratory. It is available, toxic and used as a dye for dyeing silk, cotton, wood. It is the prototype of medium-sized dyes.

Methods: Development of geopolymer based on Benin clay: Extraction of kaolin from the clay taken: The samples taken are freed of impurities using a classic method. They were first crushed and then sieved before the clay fraction was extracted after decarbonation.

Grinding–sieving: The raw clay sample collected was ground in an agate mortar and sieved at 250µm. At the end of this operation, coarse impurities such as quartz and carbonates are removed from the product.

Decarbonation: It makes it possible to eliminate all existing carbonate phases or to make their presence in the raw sample negligible in order to release the clay particles and allow their subsequent suspension.

Extraction of the clay fraction: The recovered sample is washed several times in order to obtain the fraction less than 2 µm or clay phase. The recovered fraction is dried in the oven at 105°C for two hours, crushed and preserved for further operations.

Formation of metakaolin: This operation goes through the following steps: i. Calcination of the kaolin at 800°C for 2h to allow the dehydroxylation of the kaolin which will be made more reactive[32]. ii. Grinding the metakaolin obtained in a mortar.

Formation of geopolymer from metakaolin: Three alkaline activator solutions of 130mL are prepared according to a molar ratio $n(NaOH)/n(NaAlO_2)/n(Na_2SiO_35H_2O) = 0.3/0.3/ 0.8$ [32,33].

After 10 minutes of stirring, 0.5g of CTAB and 1.5g of metakaolin are added. The suspension is stirred at room temperature for suitable times of 24 hours, 48 hours and 72 hours to obtain the geopolymers named Eti24, Eti48 and Eti72. Each geopolymer obtained underwent a series of washes by centrifugation/mixing with distilled water until the supernatant had a neutral pH. Each precipitate obtained is dried in the oven at 65°C for 24 hours then ground into a fine powder.

Characterization of materials: X-ray diffraction (XRD) analyzes of the Etigbo clay and geopolymer samples were carried out (Figure-1 and 2) in a laboratory in Italy on a Synchrotron elettra Italy brand device on a beam line MCX (Material Crystallography by X-ray) for the determination of the crystal structure. This device was used under wavelength radiation (λ=1.033Å). The diffraction patterns of the adsorbent materials were produced using the Origin 7 software for the superposition of the characterized graphs.

Evaluation of the adsorption capacity of Methylene Blue in the laboratory using the geopolymers developed: Methylene blue solution preparation: MB is acquired with a purity of 82%. A stock solution of $1000 mg.L^{-1}$ was prepared by dissolution of 1219.5mg of dye in one liter of distilled water.

Absorption of methylene blue: The stock solution was diluted in distilled water to obtain experimental solutions at the desired concentrations.

Thus, different concentrations of colored solutions (5;10;15;20;30;50;100 ppm), were prepared by proceeding by dilution using distilled water and according to the dilution equation $C_1.V_1=C_2.V_2$, with: i. C_1: concentration of the stock solution (in mg/L); V_1 : volume of the stock solution to take (in mL), ii. C_2: concentration of the daughter solution (in mg/L); V_2: volume of the daughter solution (in mL).

The diluted solutions thus prepared are then analyzed by spectrophotometry.

The residual concentrations (Ce) of the MB are determined from UV adsorption, at the wavelength λ max= 665nm on a spectrometer (NACH LAN'E DR 3900).

For each parameter measured, three or four tests were done. The average values of these tests as well as the standard deviations were calculated. The results of these different parameters studied are presented based on average values.

Analysis methods: Several concentrations of colored MB solutions (5; 10; 15; 20; 30; 50; 100 ppm) were prepared and analyzed by spectrophotometry.

The residual concentrations (Ce) of the MB are determined from UV adsorption, at the wavelength λ max= 665nm on a spectrometer (NACH LAN'E DR 3900). A calibration curve is then established at 665nm, (Figure-3), to derive a relationship between the absorbance and the MB concentration in aqueous solution. The deduced equation is of the form: Abs = 0.0372*Ce + 0.1293 (1). The adsorption tests of methylene blue by the geopolymer named Eti24 were evaluated by successively evaluating the effects of mass, aqueous medium pH and the adsorption kinetics.

Effect of adsorbent mass: The tests were carried out by stirring 100mL of BM solutions at 50ppm, with different masses (10 to 100mg) of Eti24 geopolymers, in 250mL beakers, under constant stirring at 165 rpm -1 for 48 hours, at 25°C. Volumes of each sample were withdrawn, centrifuged using the "VWR, Compact Star CS 4" centrifuge at a speed of 2500 rpm for a period of 5 min and filtered. The residual concentration (Ce) of the dye was determined, after reading the absorbance using the spectrophotometer (DR 3900), at the appropriate wavelength (λmax = 665 nm) using equation (1).

The adsorption rate of the masses of geopolymer introduced is evaluated using the formula:

$$\mathrm{R}(\%) = \frac{C_o - C_e}{C_o} \qquad (2)^{34};$$

Co is the initial ppm concentration of methylene blue and Ce, the equilibrium concentration in ppm, 48 hours later; likewise, the adsorption capacity of MB by the geopolymer is evaluated by the formula:

$$\mathrm{Qe} = \frac{(C_o - C_e)\mathrm{x}V}{m} \qquad (3)^{35};$$

m being the dry mass of adsorbent in mg and V the volume in mL of the MB solution used

By plotting the graph of the adsorption percentage relatively to the mass of adsorbent (Figure-4), the maximum mass of adsorbent was set *at* 70 mg.

Effect of pH in an aqueous medium: The effect of pH was studied using a "WTW, pH 3110" pH meter. Geopolymer samples (Eti24), with masses all equal to 0.07g, were mixed with 100mL volumes of (BM) solutions at 50ppm, in 250mL beakers. The pH of the solutions was adjusted to a range from 2 to 12 by adding either a few drops of concentrated 0.1 M hydrochloric acid or 0.1 M sodium hydroxide solutions.

Determination of the zero point of charges pHpzc: To determine the PZC pH, the method of Crini and Badot[36] was used. In each beaker, the optimal mass of geopolymer (0.07g) was added. The suspensions were kept constantly stirring, at room temperature, for 48h, in order to determine the final pH. The point of intersection between the curve and the line with equation y = x indicates the pH pzc. One author reported that at higher solution pH (pH ≥ pHpzc), geopolymers are likely negatively charged and enhance the adsorption of positively charged dye cations through electrostatic attractive forces[37].

Adsorption kinetics: The kinetics tests were carried out by mixing volumes of 100mL of BM at concentrations of 5; 10; 20; 30; 50ppm, wit masses of 0.07g of Etigbo 24h geopolymers (Eti24) at 25°C. Samples were taken at different time intervals and the residual concentration of MB in each solution was determined.

For the study of adsorption kinetics, Lagergreen models of pseudo 1st order type and pseudo 2nd order type were used. The equations of these models are: i. For pseudo-prime type kinetics order:

$$\ln(\mathrm{Qe} - \mathrm{Qt}) = \ln \mathrm{Qe} - \mathrm{Kt}$$

$$\text{Or: } Q_t = Qe[1 - \exp(-k * t)] \qquad (4)^{38}$$

Where: Qe and Q_t are the adsorption capacities in $\mathrm{mg.g^{-1}}$ respectively at equilibrium and at time t; K is the coefficient ($\mathrm{min^{-1}}$).

For pseudo-second order kinetics:

$$\frac{t}{Q} = \frac{1}{K' Q_e^2} + \frac{t}{Qe} \qquad (5)^{39}$$

With Qe and Q, the adsorption capacities in $\mathrm{mg.g^{-1}}$ respectively at equilibrium and at time t. K is the coefficient (g/mg.min), or the nonlinear equation

$$Q_t = \frac{k * Q_e^2 * t}{1 + k * Q_e * t} \qquad (6)^{39}$$

Adsorption isotherm: Kinetic tests were carried out by mixing volumes of 100 mL of BM (10 to 150 ppm) with masses of 0.07 g of geopolymers (Eti24) at 25°C. The mixture is stirred at 165 rpm for 180 minutes. Samples of each sample were taken, centrifuged and filtered.

The Langmuir and Freundlich models were applied to this adsorption equilibrium and each isotherm characteristic parameters were determined.

The modeling of MB adsorption isotherm by the Langmuir model is obtained from the nonlinear equation

$$\mathrm{Qe} = \mathrm{Qe} = \frac{q_{max}.K_L.C_e}{1 + K_L.C_e} \qquad (7)^{40}$$

Where: Ce: residual concentration of the solute at equilibrium in the solution (mg/L or in ppm). Qe: quantity of solute adsorbed per unit mass of adsorbent at equilibrium (mg/g). q_{max}: maximum solid adsorption capacity (mg/g). $K_{L:}$ Langmuir constant is a function of the adsorption energy depends on the temperature and increases with the force of interaction between the adsorbate and the surface of the adsorbent (L / mg).

The Freundlich model implies that the energy distribution for the adsorption sites is exponential. Its equation is:

$$Qe = K_f .(Ce)^{1/n} \quad (8)$$ [41]

Where: Qe: quantity of substance adsorbed per unit mass of adsorption expressed in mg/g. Ce: equilibrium concentration of the substance dissolved in the solution in mg/L. K_f: adsorption constant linked to the binding energy and expressed in $mg^{(1-n)}$. $L^{n.g-1}$. n: dimensionless constants indicating the intensity of adsorption. This is the heterogeneity factor and its value is generally between 2 and 10.

Methylene blue adsorption isotherm was modelled using Langmuir and Freundlich models from equations (6) and (7).

Results and Discussion

Characterization of the clay material and the geopolymers produced: Characterization of Etigbo clay: The determination of the mineralogical composition of the Etigbo clay material is carried out by X-ray diffraction (Figure-1). Analysis of this diagram shows the presence of kaolinite in all solids with variable proportions. The presence of kaolinite and quartz was well confirmed.

Chemical analysis: The Table below presents the chemical composition of a clay sample from Etigbo. Analysis of these data shows that silica and alumina are the major oxides in the sample, which means that it is an aluminosilicate.

The silica/alumina ratio is 1.2 for this sample, which is very close to that of pure kaolins (1.1)[42]. This result is consistent with that obtained by an author with Etigbo clay[43].

Characterization of the geopolymers produced: Figure-2 shows X-ray diffraction curve of geopolymers produced. The diffractograms show a bump around 2 theta = 20° indicating an amorphous structure for all samples.

The small peaks observed mark the presence of impurities in places, due to the presence of a few traces of other particles such as sodium which were not completely eliminated during the series of washing the geopolymers with distilled water.

Methylene blue adsorption results: Effect of the mass of the adsorbent: The influence of the mass of the adsorbent was studied in the interval 10 mg–100 mg. The curve in Figure-4 shows that the efficiency of MB removal increased from 13.08% to 47.01% for a mass of adsorbent varying from 10 to 30 mg respectively then from 72.11% to 81.20% with an increase in adsorbent mass from 40 to 70 mg. It then remains almost constant beyond that. This is due to the increasing of available adsorption sites with adsorbent dosage. However, the increase in sites had little effect on the efficiency of MB removal for an increase in adsorbent mass (beyond 70 mg), due to the establishment of a equilibrium at a low concentration of adsorbate in the solution. A mass of 0.07 g of geopolymers is then capable of fixing a maximum dye of around 81%. In order to find the adsorption capacities by saturating all the probable sites, we have chosen to work with adsorbent masses of 0.07 g in the rest of this work.

Effect of pH on the elimination of the dye: The influence of the initial pH of the solutions on the adsorption was studied in the range from 2 to 12. The amounts of dye retained by the adsorbent from different solutions were found to be closely related to the initial pH value of the solution (Figure-4).

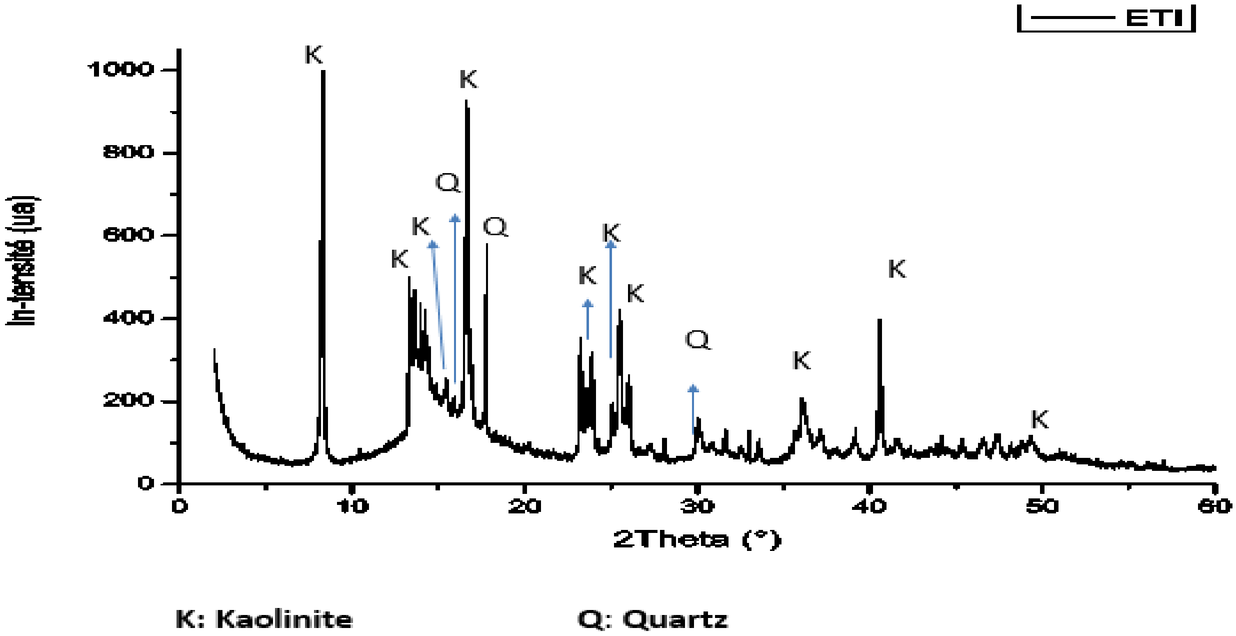

Figure-1: X-ray diffraction (XRD) patterns of a clay sample from Etigbo.

Table-1: Chemical analysis of a sample of Etigbo clay.

Chemical element	If	Al	Fe	CaO	Mg	K	N / A	S	CO2 _	Total
Content (%)	44.56	37.60	2.22	0.00	0.31	0.28	0.00	0.00	14.60	99.57

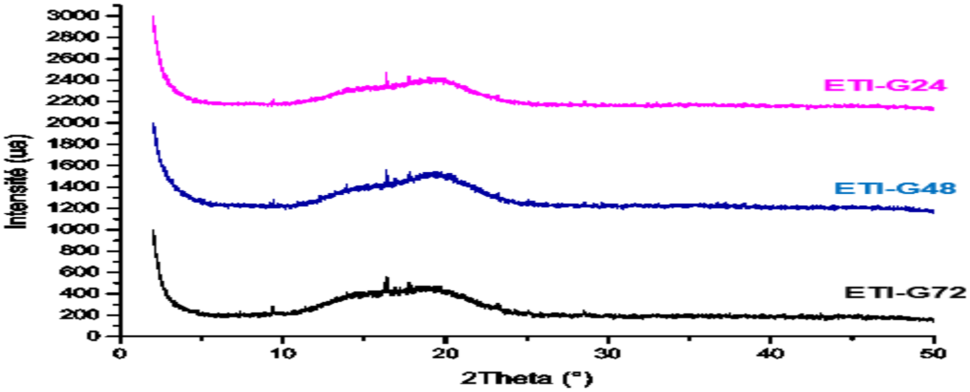

Figure-2: X-ray diffraction (XRD) patterns of the Eti24, Eti48 and Eti72 geopolymers developed.

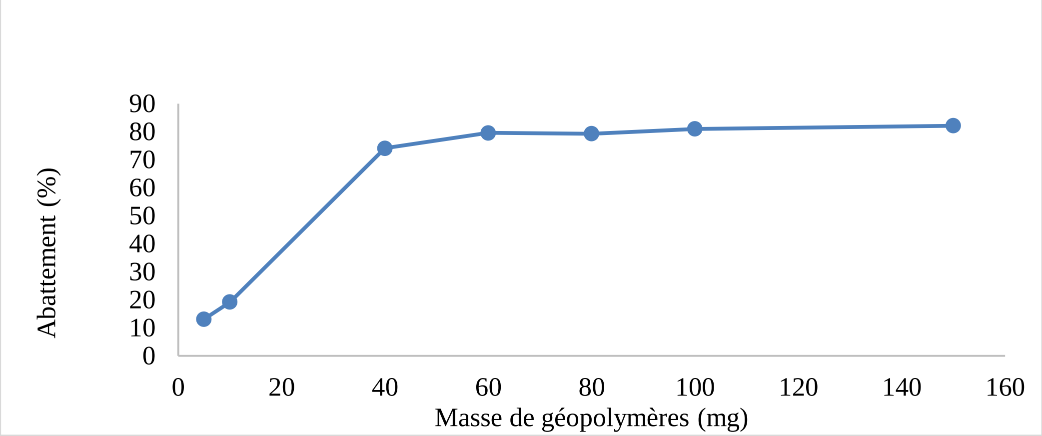

Figure-3: Effect of geopolymer mass.

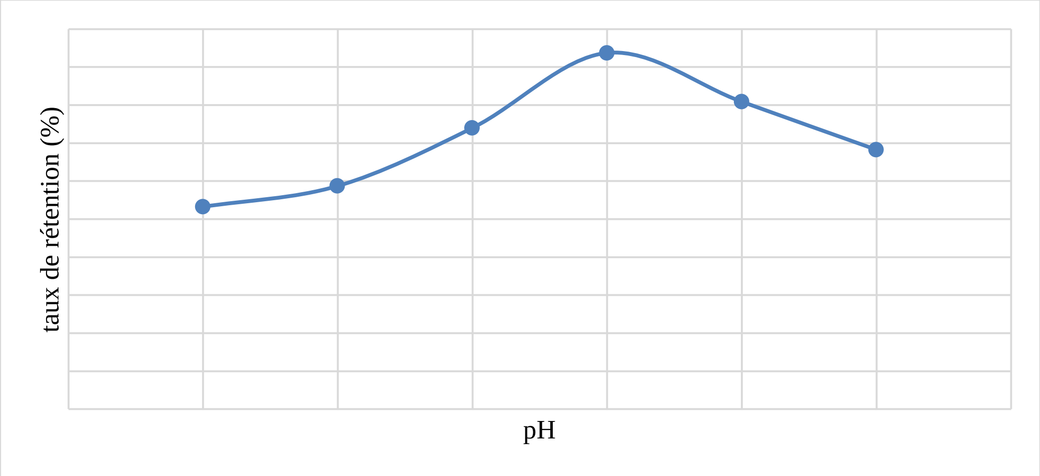

Figure-4: Effect of pH.

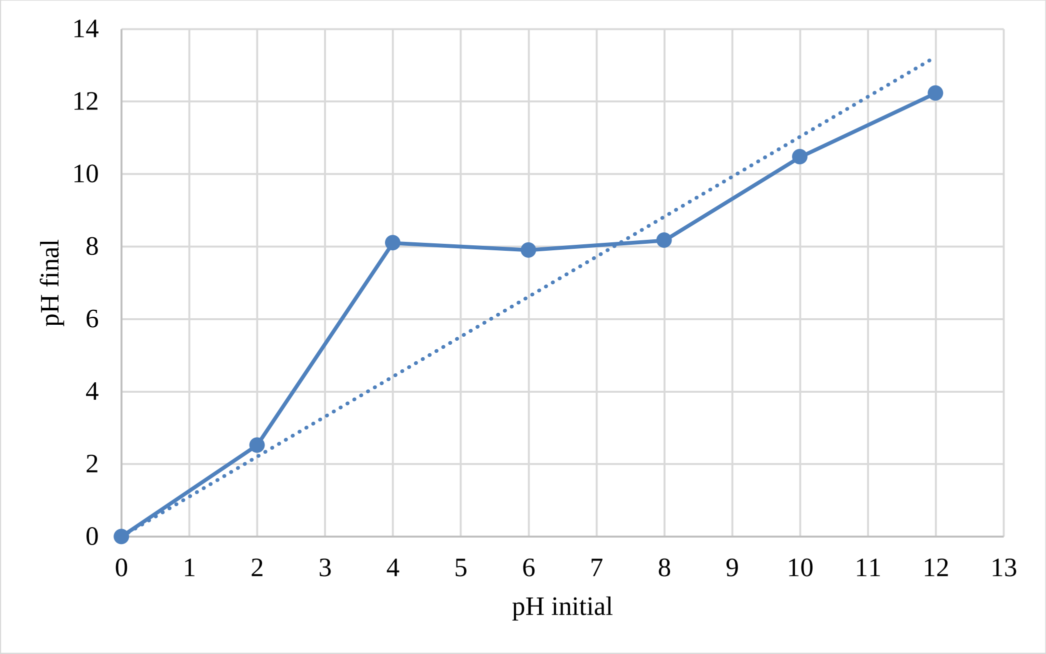

Figure-5: Determination of pH pzc.

It appears from the results obtained that: i. Adsorption increases with pH up to pH=8, ii. Adsorption is particularly disadvantaged at too high pH (pH › 8).

These developments can be explained as follows: i. At low pH: there is an anion exchange capacity in the adsorbent: therefore, anions be more attracted towards the surface, which disadvantages the adsorption of the cationic MB. ii. At high pH, exchange capacity of cation develops: OH^- binds more and develops a negative charge, so that cations in solution are in turn attracted to the surface of the adsorbent, promoting the adsorption of cationic B.M. Ofomaja noticed in 2007 that the retention of MB on an adsorbent increases with the negative surface charge[44].

Knowing that pH_{PZC} of the geopolymer is approximately equal to 7.2, the charge on its surface is positive below 7.2 (pH less than 7.2) and negative beyond (pH › 7,2) . In the latter case, the MB molecules (cationic species) will have to be more and more adsorbed going from pH 2 to 7.2; this is what justifies the increase in the adsorption rate from 53.24% to 93.72% for pH values ranging from 2 to 8. iii. The reduction in the adsorption of MB at too high pH values (pH › 8) could be due to a probable competition between the Na^+ cations of NaOH, which are smaller and more mobile than those of the dye, preventing them from accessing the surface of the adsorbent.

Determination of the zero point of charges pH PZC: To understand the action of the net charge of the geopolymer surface in the fixation of the dye, we determine the zero-charge point (pH PZC). Figure-5 shows that the PZC pH of the geopolymer is approximately equal to 7.2.

As the dye used is basic, its dissolution in water releases positively charged colored ions (cations). The geopolymer contains polar groups such as hydroxyls and carboxyls, therefore the electrical charge of the adsorbent depends on the pH of the medium, due to the ionization of these surface functional groups.

It has been reported that the retention of MB on a biosorbent rises with increasing surface negative charge[43]. This explains that retention is more remarkable when the pH exceeds the value of 7.2.

With regard to industrial effluents whose pH is around 7 or more, the adsorption rate of MB would be at least 85% for the adsorbent since a cation exchange capacity develops depending on whether the medium is more basic. So the adsorption of MB would be very favorable.

Evaluation of the decolorization capacities of geopolymers: MB adsorption kinetics for different concentrations: Initial MB concentration influence on the retention rate at different contact times is shown in Figure-6. For the five concentrations used (5, 10, 20, 30 and 50ppm), the retention rate increases with the increase in reaction time following two different slopes. The first is rapid and takes place in the first 15 minutes approximately while the second, beyond 15 minutes, is slow and could express the balance between the fractions of dye retained and those desorbed. Overall retention is comparable for the five concentrations with yields of 61.99; 76.43; 86.87; 85.33; 92.08 respectively. Thus the retention rate increases as the initial concentration increases.

We can therefore remember that: i. The equilibrium time, corresponding to the time of the maximum stable adsorption point and identical to each of the curves drawn, is 120 minutes. Generally equilibrium times depend on the raw material used and the dye. Indeed, it has been reported that the adsorption equilibrium time of MB by *Posodonia oceanica fibers* is 10 min while for this same dye the adsorption equilibrium time is 45 min for the releases of grapefruit[46.47]. Adsorption for the different concentrations is rapid within the first 15 minutes. This could be due to the abundance of adsorption sites from the start of the tests. As these are filled, the phenomenon is reduced, until it stabilizes after 120 minutes because the remaining surface sites are difficult to occupy. This is in agreement with the results of other researchers in the literature[24,48]. ii. Lagergreen's models of adsorption kinetics of the pseudo 1st order type and then that of the pseudo 2nd order type were explored**.**

All the kinetic parameters are determined using the Origin Pro 2022 software and recorded in Table-2; we find the adsorption coefficients according to these models as well as the equilibrium adsorption capacities (Qe), the experimental values being respectively 4.428; 10.918; 23.936; 37.492; 65.922 for the different concentrations ranging from 5ppm to 50ppm**.**

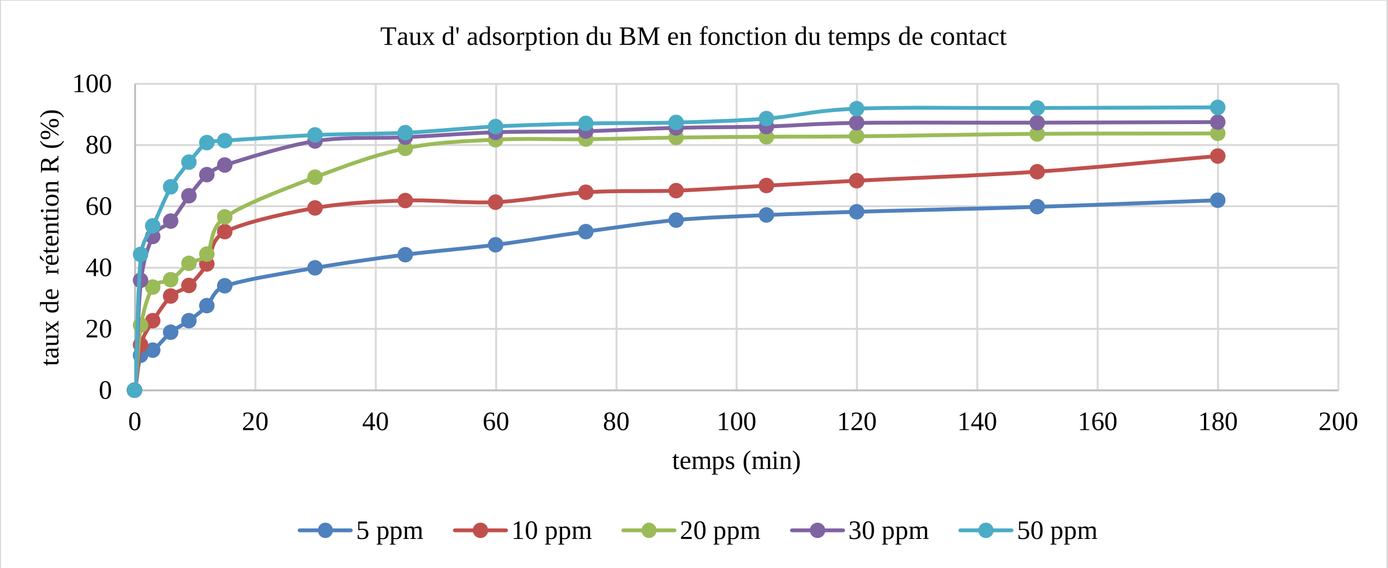

Figure-6: Adsorption rate of Eti24 geopolymer for various MB concentrations as a function of time.

Table-2: Rate constants and possible kinetic models of geopolymer adsorption.

Pseudo 1st order reaction				
Co(ppm)	R2 $^{-}$	K (min $^{-1}$)	Qe (mg/g)	Qexp
50	0,924	0,353±0,058	61,349±1,480	65,922±7,0711E^{-4}
30	0,916	0,224±0,035	35,678±0,991	37,492±7,0711E^{-4}
20	0,948	0,088±0,010	23,355±0,650	23,936±7,0711E^{-4}
10	0,958	0,920±0,010	9,550±0,244	10,918±0,000
5	0,950	0,053±0,007	3,996±0,131	4,428±9,574E^{-4}
Réaction pseudo 2nd ordre				
Co(ppm)	R^2	[K' (g/mg.min)]	Qe (mg/g)	Qexp
50	0,978	0,010±0,001	63,954±0,924	65,922±7,0711E^{-4}
30	0,977	0,011±0,001	37,286±0,609	37,492±7,0711E^{-4}
20	0,960	0,00585±9,31858E^{-5}	25,060±0,044	23,936±7,0711E^{-4}
10	0,979	0,012±0,001	10,492±0,238	10,918±0,000
5	0,980	0,014±0,002	4,604±0,133	4,428±9,574E^{-4}

The correlation coefficients (R^2) for these two models are much better shown by the second model, giving a better description of the kinetics of the adsorption reaction, because the R^2 values obtained for the pseudo-first kinetics model are lower than those of the pseudo-second kinetics model.

The equilibrium adsorption capacities (Qe) calculated using this model is also very close to the experimental ones (Qexp) found. This is not the case for the pseudo 1st order type adsorption model. We can therefore say that the adsorption of MB by the Eti24 geopolymer follows a pseudo 2nd order kinetic model. Several authors have reported similar results for the adsorption of MB on different adsorbents[49,50]. It can be concluded that the second-order equation is a better fit to the adsorption data than the first-order model.

Modeling of the adsorption isotherm: Figure-7 shows, at constant temperature, the relationship between the adsorption capacity at equilibrium (Qe) and the concentration of MB in solution (Ce) called the adsorption isotherm. The appearance of this adsorption equilibrium isotherm is that of the L-type isotherm. The Freundlich and Langmuir models were used to interpret the adsorption phenomenon of MB on Eti 24 geopolymer.

Langmuir model: The modeling of MB adsorption isotherm by the Langmuir model **is** shown in Figure-8[40]. **Freundlich model:** The modeling of the adsorption isotherm of methylene blue by the Freundlich model is shown in Figure-9[41] .

Figures-8 and 9 respectively represent the Langmuir and Freundlich adsorption isotherms for the adsorption of methylene blue on the Eti24 geopolymer. The constants characterizing each of the systems were determined and entered in Table-3. The best correlation of the experimental results is obtained with the Freundlich model. It can be deduced that the most ideal model to define MB adsorption is that of Freundlich. According to Freundlich's hypotheses, we can say that the adsorption took place on heterogeneous surfaces because these sites are not all equivalent, they have different adsorption energies.

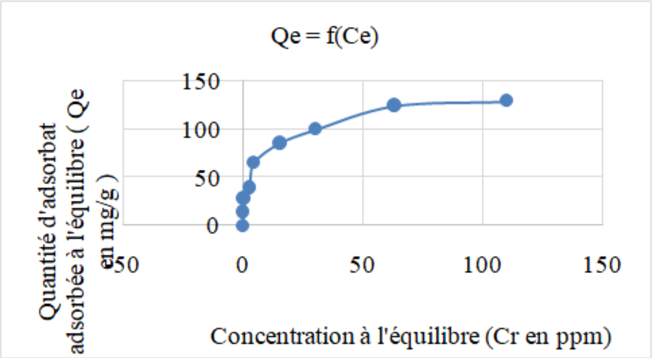

Figure-7: The adsorption equilibrium isotherm: (m = 70 mg; V = 100 ml; t = 180 min).

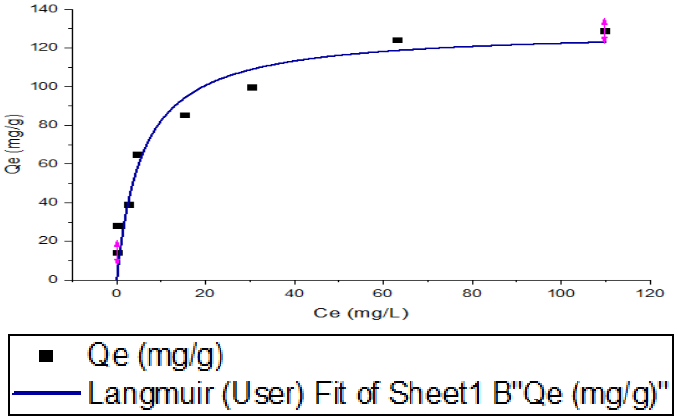

Figure-8: Langmuir model for the adsorption of methylene blue by the Eti24 geopolymer.

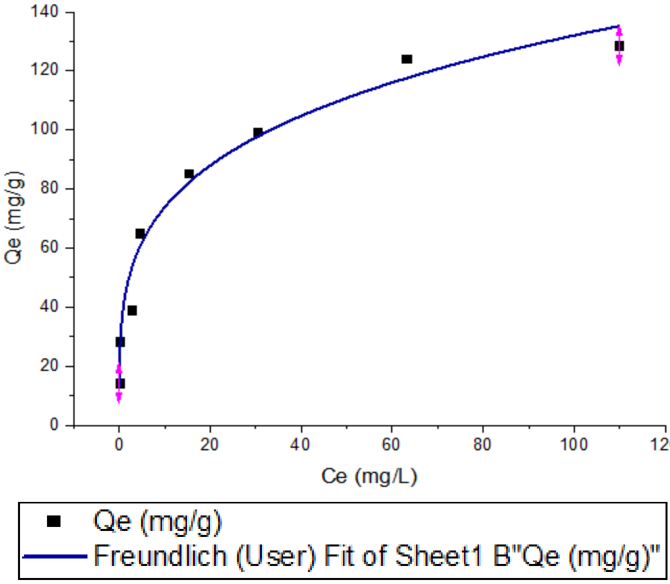

Figure-9: Freundlich model for the adsorption of methylene blue by the Eti24 geopolymer.

Conclusion

For the adsorption of MB, a good result was obtained for a contact time of 120 minutes and a mass of adsorbent of 70mg. With an adsorption rate of at least 85% at pH ≥ 7, the maximum adsorption capacity determined by the Langmuir model is 129.41mg/g. The Freundlich model better describes the adsorption isotherm and the adsorption kinetics is pseudo-second order.

This study showed that the clays of Kétou in general and those of Etigbo in particular which have very little economic activity can be good raw materials for the synthesis of geopolymers for an adsorption application on MB from water contaminated. Thus, a great contribution to the protection of the environment, in particular to the purification of water and the valorization of Beninese clays was highlighted during this work.

Table-3: Langmuir and Freundlich equilibrium constants for the adsorption of methylene blue on the Eti24 geopolymer and at different equilibrium concentrations.

Langmuir model		Freundlich model	
qmax	129,40684±10,97584	K_f	41,29991±3,65715
k	0,17511±0,06479	n	3,96201±0,3651
R^2	0,91581	R^2	0,97628

We plan to subsequently study the regeneration of the clay surface or the incorporation of a step of degradation of organic pollutants.

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