Research Article

Use of a Clay from Southern Ivory Coast (Bingerville) for the Adsorption of Methyl Orange in Aqueous Media

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Abstract

Increasing levels of textile dyes being discharged into the environment as industrial waste represent a serious threat to human health, life, resources and ecological systems. It is therefore necessary to treat wastewater from textile industries before discharging it into the environment. The aim of this project is to eliminate methyl orange (MO) from textile industry wastewater using clay from Bingerville (Ivory Coast). The clay used was characterized by Scanning Electron Microscopy, Brunauer-Emmett-Teller and pH of Zero Charge. MO concentration was monitored using a UV-visible spectrophotometer. Characterization of the clay by SEM and BET showed that our clay is microporous. The study showed that the surface of our clay has a pH of zero. Adsorption of methyl orange on our clay reaches adsorption equilibrium in 60 minutes. The adsorption model corresponds to the pseudo-order 2 kinetic model. Two adsorption isotherm models (Langmuir and Freundlich) are applicable to the adsorption of our dye on clay. This implies that the dye adsorption process on our clay is governed by a bimolecular process involving a collision between an active site on the clay and a dye molecule. Bingerville clay can be used to effectively treat dye-contaminated wastewater, since the maximum adsorbed quantity is equal to 58.139 mg g^{-1}. The best adsorption rate was obtained in acid medium (pH = 2.26) with an adsorption rate of 91.84%.

Keywords

Methyl Orange, Clay, Adsorption, Kinetics

1. Introduction

Many organic compounds are essential to life. However, these compounds become toxic for the environment and living beings when their concentration is high in wastewater [1-3]. The majority of these toxic compounds come from various industrial wastes [1, 2], including water from the textile in-dustry. However, in general, wastewater from our country's textile industries containing toxic dyes is not treated before being discharged into our waterways and the environment. Among these toxic dyes is methyl orange, which can directly harm living organisms and the environment. This constitutes a

real danger for living beings and the environment. It is therefore essential to treat wastewater before discharging it into the environment.

In the literature, several treatment methods exist, including extraction, incineration, chemical and biological methods, electrochemical methods and adsorption [4-9]. Among these methods, adsorption is one of the most effective and economical, with a high potential for removing organic compounds, dyes and metals from water [5, 6]. Clay, an inexpensive adsorbent, is the focus of particular attention in the adsorption of dyes and many other pollutants contained in wastewater [10-12]. These properties are further enhanced by activation processes such as chemical activation, which involves contacting the clay with a strong acid (hydrochloric acid) [13].

The aim of this work is to use natural clay from Bingerville (southern Ivory Coast) activated with hydrochloric acid to remove methyl orange from wastewater.

2. Materials and Methods

2.1. Clay Activation

The clay was first crushed and sieved with a 100 μm sieve; it was then placed in contact with distilled water for 24 hours. The clay is then filtered and dried in an oven for 24 hours at 60 ℃. 0.1 L of 1 M hydrochloric acid is added to 5 g of dried clay. The mixture is stirred for 24 hours. After 24 hours stirring, the mixture is filtered and dried for 24 hours in an oven at a fixed temperature of 60 ℃. The clay is then washed thoroughly with bi-distilled water until a neutral pH is reached. The clay is dried for a final 24 hours. Finally, the sample is stored in airtight jars.
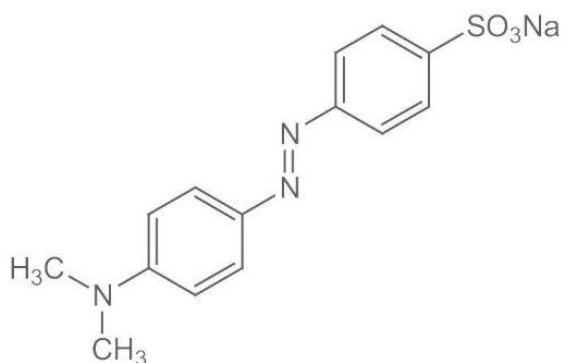
2.2. Adsorption Study

Figure 1. MO molecule.

A 100 mg L^{-1} stock solution of MO (analytical grade, Sigma-Aldrich®) was prepared from a commercial solution of MO (C. I Acid Orange 52). Figure 1 shows the

semi-developed formula of MO. The solutions studied were prepared by successive dilutions of the stock solution. A 1 M hydrochloric acid solution (Suprapur Merck) and a 1 M sodium hydroxide solution (Prolabo) were used to adjust pH. All solutions were prepared with distilled water at 25 ℃. The resulting suspension was analyzed for residual concentrations using an AL 800 UV-Visible spectrophotometer (Aqualytic).

The amount of methyl orange adsorbed was determined using relationship (1):

$$q_t = \frac{C_0 - C_t}{m} \times V \tag{1}$$

With:

q_t: quantity of MO adsorbed per unit mass of clay (mg g^{-1})

C_0: MO concentration before adsorption (mg L^{-1})

C_t: remaining MO concentration at time t (mg L^{-1})

V: volume of MO solution (L)

m: mass of activated clay (g)

Relation (2) was used to determine the rate of MO adsorption on our clay:

$$\text{Adsorption rate } (\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \tag{2}$$

3. Results and Discussion

3.1. Characterization of Clay

3.1.1. Characterization by Scanning Electron Microscopy

Figure 2 show the Scanning Electron Microscopy images of the outer surface of Bingerville clay activated with hydrochloric acid. The clay is made up of microscopically planar sheets arranged parallel to one another. A few pores and micropores are present.
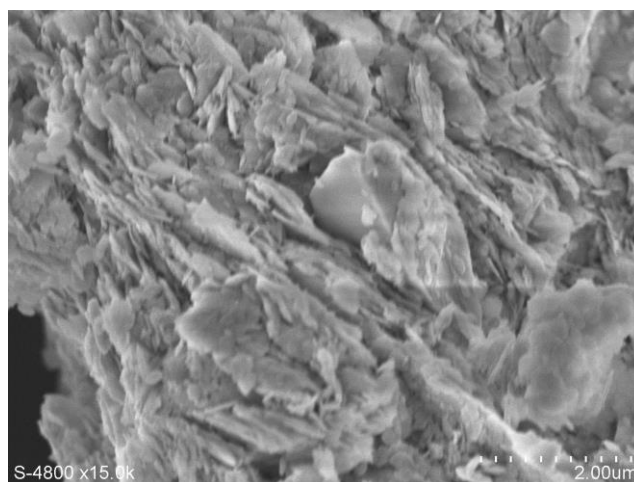

Figure 2. Scanning Electron Microscopy of Clay.

3.1.2. Specific Surface Area of Clay

Measurements of nitrogen adsorption and desorption on our clay were carried out to determine pore volume and specific surface area. Figure 3 shows the results obtained. This figure shows an experiment corresponding to a type IV adsorption isotherm based on the classification of the International Union of Applied Chemistry [14, 15]. Specific surface area, total pore volume and micropore volume are recorded in Table 1. A value of 34.879 m^2/g was obtained for the specific surface area, showing that our clay has a high specific surface area. We also note that activated clay is a microporous material (very low P/P_0 range).
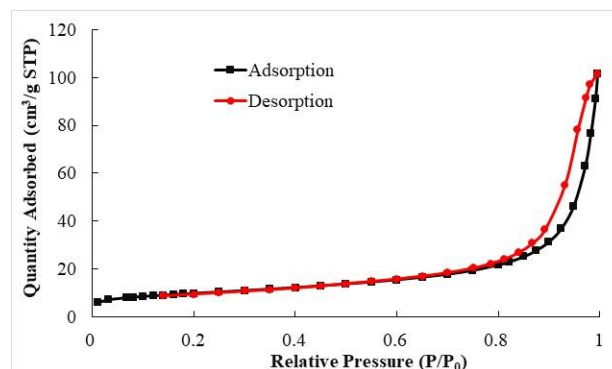

Figure 3. *Nitrogen adsorption-desorption isotherm for bingerville clay.*

Table 1. *Textural characteristics of clays.*

BET Specific surface area (m^2 g^{-1})	micro pore volume ($cm^3 g^{-1}$)	Total pore volume ($cm^3 g^{-1}$)	P/P_0= 0.971 Pore volume ($cm^3 g^{-1}$)
34.879	0.097	0.155	0.097

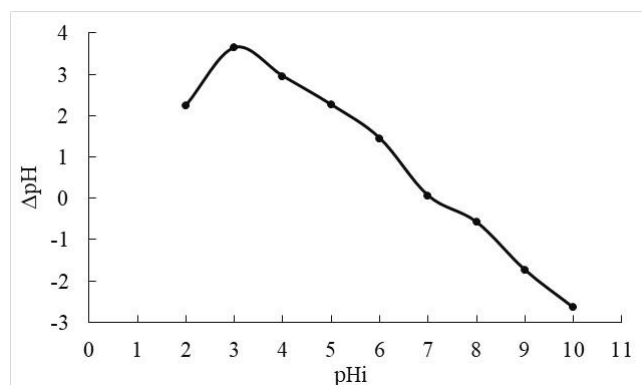### 3.1.3. pH of Zero Charge point (pHpzc)

Figure 4. *Curve of pHpzc determination.*

The pH at zero charge point corresponds to the pH of the aqueous solution when the net charge is zero at the adsorbent surface. This gives the pH of the clay. It provides information on the net charge on the adsorbent surface as a function of the pH of the solution [16]. That of our clay was determined using the curve in figure 4, which indicates that the pHpzc of our clay is equal to 7.08. This result shows that the surface of our clay is neutral. If the pH value of the medium studied is lower than pHpzc, the surface functions of our adsorbent will have an excess of protons (H^+). The clay surface will attract negatively charged compounds. However, if the pH of the medium is higher than pHpzc, the adsorbent surface will be deprotonated by OH^- ions. The clay's active surface acts as a magnet for positively charged compounds [10, 16].

3.2. Kinetic Study of MO Adsorption on Clay

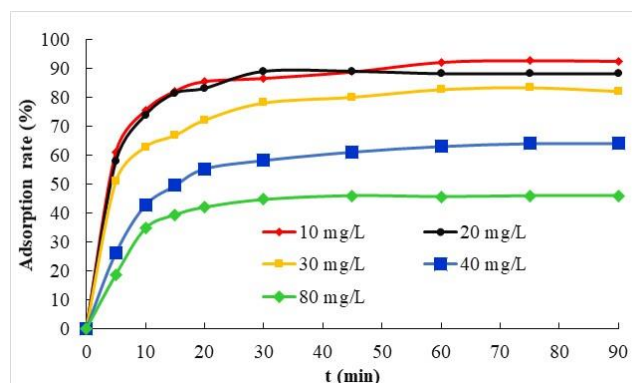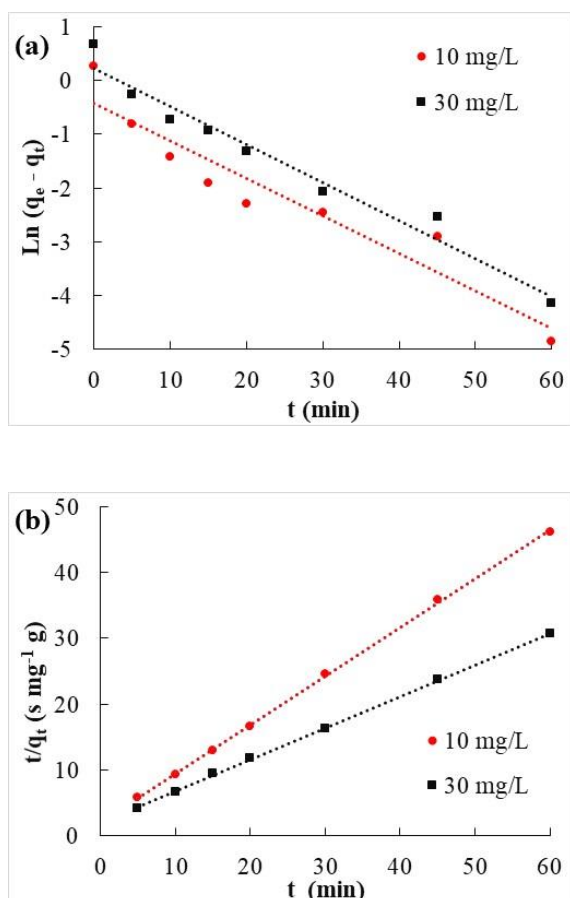### 3.2.1. Adsorption Equilibrium Time

Figure 5. *Removal efficiency of MO on clay.*

Figure 5 shows a rapid elimination of MO during the initial phase of contact time, before stabilizing. The rapid adsorption phase is due to the accessibility of the adsorbent's active sites. The majority of the adsorbent's active sites are occupied during the first adsorption stage. Adsorption then becomes slower and slower. This decrease in adsorption speed can be

explained by the reduction in the number of active sites. It can also be explained by the repulsive forces between the MO molecules already adsorbed by the clay and those present in solution. This figure shows that the equilibrium time for MO adsorption on Bingerville clay is 60 min. The adsorption kinetics of our dye on our clay studied at various concentrations shows a behavior often encountered for dye adsorption [17, 18].

3.2.2. Application of Kinetic Models

The kinetic model for dye adsorption on clay was determined by applying the pseudo-order 1 and 2 kinetic models.

Figure 6. Application of pseudo-order 1 (a) and 2 (b) kinetic models to dye adsorption on clay.

Equations 3 and 4 were used to apply pseudo-order 1 and 2 kinetic models, respectively [17, 18].

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (4)$$

With:

q_e, the quantity of methyl orange adsorbed at equilibrium in (mg/g);

q_t, the quantity of methyl orange adsorbed at time t in (mg/g);

k_1 (1/h) and k_2 (g.mg^{-1}.h^{-1}) are the adsorption rate constants.

Figure 6a and 6b show the results obtained by applying the pseudo-order 1 and 2 kinetic models, respectively. The kinetic parameters of these two models are summarized in Table 2.
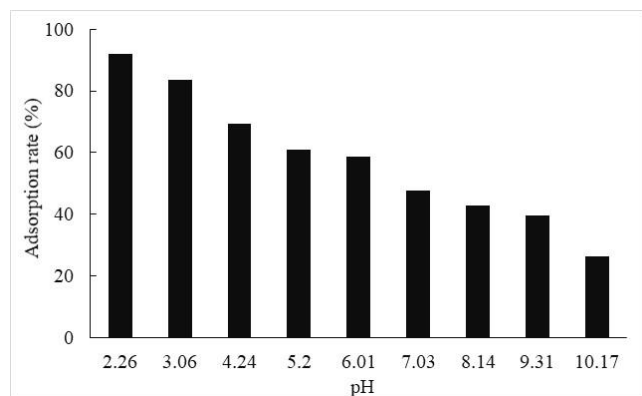
Table 2. Parameters of dye adsorption kinetics models.

Pseudo-first order	10 mg L^{-1}	k_1 (min^{-1})	0.070
		R^2	0.909
		$q_{e\ cal}$ (mg g^{-1})	0.932
		$q_{e\ exp}$ (mg g^{-1})	1.308
	30 mg L^{-1}	k_1 (min^{-1})	0.071
		R^2	0.966
		$q_{e\ cal}$ (mg g^{-1})	1.249
		$q_{e\ exp}$ (mg g^{-1})	1.974
Pseudo-second order	10 mg L^{-1}	K_2 (g m^{-1} min^{-1})	0.275
		R^2	0.999
		$Q_{e\ cal}$ (mg g^{-1})	1.347
		$Q_{e\ exp}$ (mg g^{-1})	1.308
	30 mg L^{-1}	K_2 (g m^{-1} min^{-1})	0.116
		R^2	0.999
		$Q_{e\ cal}$ (mg g^{-1})	2.084
		$Q_{e\ exp}$ (mg g^{-1})	1.974

From this summary table we note that the coefficients of determination for pseudo-2-order kinetics are higher than those for pseudo-1-order kinetics. We also note that the experimental maximum quantities of dye adsorbed per mass of clay at equilibrium are closer to the theoretical maximum values for the quantity of dye adsorbed with pseudo-2-order kinetics than with pseudo-1-order kinetics. This implies that the dye adsorption process on our clay is governed by a bimolecular process involving a collision between a clay active site and a dye molecule [18].

3.3. Effect of pH

The influence of pH on the decoloration of methyl orange by our clay was studied. The results are shown in Figure 7. It can be seen that as pH increases, the removal rate of MO decreases. These results show that acidic medium is better for methyl orange decolorization. The best adsorption rate was obtained at pH = 2.26 with an adsorption rate of 91.84%. This shows that methyl orange is an anionic dye, as clay is positively charged at acid pH. This promotes the adsorption of MO, which is an anionic dye, through electrostatic attraction. [17, 19, 20].

Figure 7. *Effect of initial pH of methyl orange solution on adsorption.*

3.4. Isotherme d'adsorption

Figure 8. *Adsorption isotherms for MO on clay.*

The adsorption isotherm for MO on clay was studied at 25 °C. Figure 8 shows the mass of MO removed per gram of clay at equilibrium as a function of equilibrium concentration. This figure shows that the mass of MO removed per gram of clay at equilibrium increases as the concentration of MO at equilibrium increases. According to the IUPAC classification, our study corresponds to the type I isotherm [21, 22]. This shows that there are strong interactions between adsorbent and adsorbate. This type of isotherm is that of physical adsorption on a microporous adsorbent. This confirms the microporous nature of clay [23]. During MO adsorption, saturation of the active sites in clay increases progressively. The Freundlich and Langmuir adsorption isotherm models were applied to the adsorption of MO on clay using relations 5 and 6 respectively [21].

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \qquad (5)$$

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m b} \times \frac{1}{C_e} \qquad (6)$$

Figure 9 shows the results obtained. The parameters of the adsorption isotherm models are shown in Table 3.

Figure 9. *Langmuir (a) and Freundlich (b) adsorption isotherm models applied to MO removal.*

Table 3. *Parameters of the Langmuir and Freundlich models.*

Langmuir			Freundlich		
R^2	q_m (mg g^{-1})	b	R^2	K_f	n
0.985	58.139	0.011	0.991	0,674	1.104

Isothermal adsorption models gave coefficients of determination of 0.985 for the Langmuir model and 0.991 for the Freundlich model. This shows that both models are applicable. The Langmuir model was used to determine the maximum amount of MO adsorbed per gram of clay. A value of 58.139 mg g^{-1} was obtained. This result indicates that Bingerville clay can be used to effectively treat dye-contaminated wastewater.

4. Conclusion

The study showed that Bingerville clay is microporous and has a neutral pH at its surface. Adsorption of methyl orange on our clay reaches adsorption equilibrium in 60 minutes. The adsorption model corresponds to the pseudo-order 2 kinetic model. Two adsorption isotherm models (Langmuir and

Freundlich) are applicable to the adsorption of our dye on clay. This implies that the dye adsorption process on our clay is governed by a bimolecular process involving a colli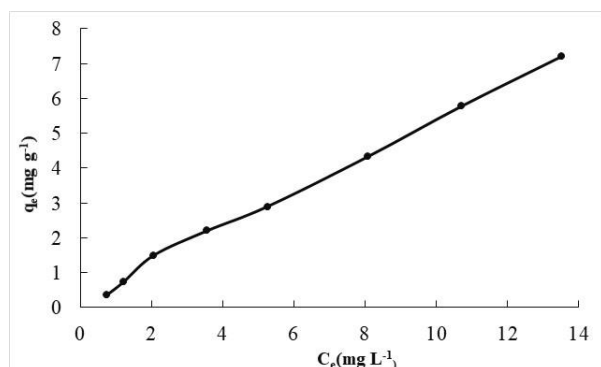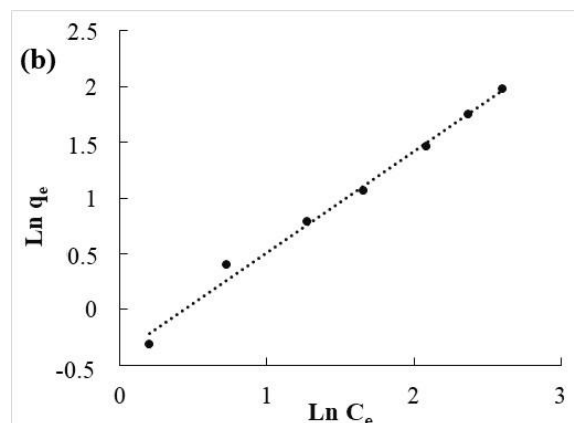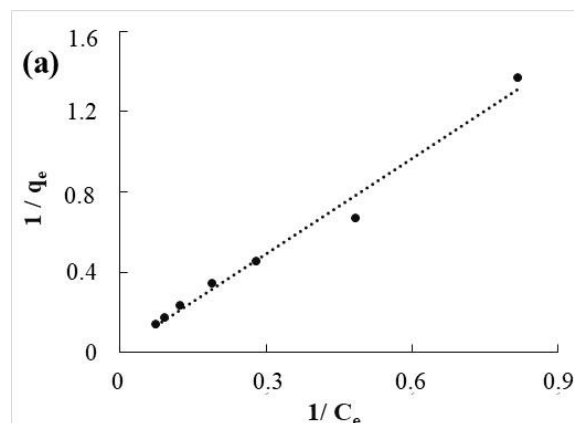sion between an active site on the clay and a dye molecule. The best adsorption rate was obtained in a very acidic environment, with an adsorption rate of 91.84%. The maximum amount of MO adsorbed by the clay was 58.139 mg g^{-1}. These results show that Bingerville clay can be used to treat wastewater from the textile industry.

Abbreviations

MO: Methyl Orange

pHpzc: pH at Zero Charge Point

IUPAC: International Union of Pure and Applied Chemistry

SEM: Scanning Electron Microscopy

BET: Brunauer-Emmett-Teller

Conflicts of Interest

The authors declare no conflict of interest.

References

[1] Thomas M., Omar H., Andreas D., Philip J. L. Soil and water pollution and human health: what should cardiologists worry about? *Cardiovascular Research*. 2023, 119(2), 440–449. https://doi.org/10.1093/cvr/cvac082

[2] Fida M., Li P., Wang Y., Alam S. M. K., Abel N. Water Contamination and Human Health Risks in Pakistan: A Review. *Expo Health*. 2023, 15, 619–639. https://doi.org/10.1007/s12403-022-00512-1

[3] Sadia S. P., Gnamba C. Q.-M., Kambiré O., Konan K. M., Berté M., Koffi K. S., Kouadio K. E., Kimou K. J., Pohan L. A. G., Ouattara L. Principal component analysis of physico-chemical parameters of wastewater from the University Hospital Center of Treichville in Côte d'Ivoire. *J. Mater. Environ. Sci*. 2023, 14(7), 826-837.

[4] Sadia S. P., Kambiré O., Gnamba C. Q.-M., Pohan L. A. G., Berté M., Ouattara L. Mineralization of Wastewater from the Teaching Hospital of Treichville by a Combination of Biological Treatment and Advanced Oxidation Processes. *Asian Journal of Chemical Sciences*. 2021, 10(2), 1-10. https://doi.org/10.9734/AJOCS/2021/v10i219086

[5] Kouassi N. L. B., Doubi B. H. G., Diabate D., Blonde L. D., Trokourey A. Recycling of Alum Sludge for Rhodamine B Removal from Industrial Effluents. *Chemistry Africa*. 2023, 6, 485–498. https://doi.org/10.1007/s42250-022-00473-7

[6] Kouassi N. L. B., N'goran K. P. D. A., Blonde L. D., Diabaté D., Trokourey A. Simultaneous Removal of Copper and Lead from Industrial Effluents Using Corn Cob Activated Carbon. *Chemistry Africa*. 2023, 6, 733–745. https://doi.org/10.1007/s42250-022-00432-2

[7] Kouakou J. K., Ollo K., Sylvestre K. K., Souleymane K., Lassiné O. Voltammetric and chronoamperometric study of omnipaque electrooxidation at Ti/RuO$_2$ electrode. *RAMReS Sciences des Structures et de la Matière*. 2022, 6(1), 47-62.

[8] Kambiré O., Sadia S. P., Kouakou Y. U., Pohan L. A. G., Koffi K. S., Kouadio K. E., Kimou K. J., Koné S., Lassiné O. Kinetic of the Oxygen and Chlorine Evolution Reaction on Platinum Electrodes at Neutral pH. *Asian Journal of Research in Chemistry*. 2022, 15(3), 213-219. https://doi.org/10.52711/0974-4150.2022.00037

[9] Kambiré O., Chia Y. P. A., Kouakou Y. U., Yeo F., Lassiné O. Photocatalytic degradation of methyl orange in an aqueous solution in presence of copper oxide. *Journal of Chemical, Biological and Physical Sciences. Section A: Chemical Sciences*. 2023, 13(4), 401-412.

[10] Lébé P. M.-S. K., Daouda K., Max R. W. M., Aliou G. L. P., Gaoussou C., Léon K. K., Jonas Y. A.-Y. Use of two clays from Côte d'Ivoire for the adsorption of methyl red from aqueous medium. *Chemical Physics Letters*. 2023, 810, 140183. https://doi.org/10.1016/j.cplett.2022.140183

[11] Bintou C., Lemeyonouin A. G. P., Ollo K., Lébé P. S. K., Hervé G.-D., Donourou D., Lassiné O. Valorization of Green Clay from Bouaflé (Ivory Coast) in the Simultaneous Elimination of Organic Pollutants and Metallic Trace Elements by Adsorption: Case of Methylene Blue and Cadmium Ions. *Chemical Science International Journal*. 2020, 29(8), 37-51. https://doi.org/10.9734/CSJI/2020/v29i830200

[12] Teğin İ., Batur M. Ş., Yavuz Ö., Saka C. Removal of Cu (II), Pb (II) and Cd (II) metal ions with modified clay composite: kinetics, isotherms and thermodynamics studies. *Int. J. Environ. Sci. Technol*. 2023, 20, 1341–1356. https://doi.org/10.1007/s13762-022-04028-8.

[13] Koffi J. B. A., Tchirioua E., Lynda E., Olivier L. Adsorption of lead on a natural clay from the Agboville region (Côte d'Ivoire) and activated clay with hydrochloric acid. Modeling by linear isotherms of langmuir and freundlich. *RASĀYAN Journal of Chemistry*. 2020, 13(3), 1933-1943. http://dx.doi.org/10.31788/RJC.2020.1335504

[14] Thommes M., Kaneko K., Neimark A. V., Olivier J. P., Rodriguez-Reinoso F., Rouquerol J., Sing K. S. W. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). *Pure and Applied Chemistry*. 2015, 87, (9-10), 1051-1069. https://doi.org/10.1515/pac-2014-1117

[15] Rahimi K., Riahi S., Abbasi M., Fakhroueian Z. Modification of multi-walled carbon nanotubes by 1,3-diaminopropane to increase CO$_2$ adsorption capacity. *Journal of Environmental Management*. 2019, 242, 81-89, https://doi.org/10.1016/j.jenvman.2019.04.036

[16] Abo E. A., Yobouet Y. A., Kouakou Y. U., Trokourey A. Optimisation de la préparation de charbons activés à base d'épis de maïs et caractérisation physico-chimique. *International Journal of Innovation and Applied Studies*. 2020, 29(4), 1161-1171.

[17] Kambiré O., Kouakou Y. U., Kouyaté A., Sadia S. P., Kouadio K. E., Kimou K. J., Koné S. Removal of rhodamine B from aqueous solution by adsorption on corn cobs activated carbon. *Mediterranean Journal of Chemistry*. 2021, 11(3), 271-281.: http://dx.doi.org/10.13171/mjc02112131596ollo

[18] Abollé A., Kouakou Y. U., Kambiré O., Koné Y. T., Kouakou A. R. Adsorption of Methyl Orange on Corncob Activated Carbon: Kinetic, Equilibrium, and Thermodynamic Studies. *Earthline Journal of Chemical Sciences*. 2022, 8(2), 205-224. https://doi.org/10.34198/ejcs.8222.205224

[19] Abida K., Munawar I., Anum J., Kiran A., Zill-i-Huma N., Haq N. B., Shazia N. Dyes adsorption using clay and modified clay: A review. *Journal of Molecular Liquids*. 2018, 256, 395-407. https://doi.org/10.1016/j.molliq.2018.02.034

[20] Brahim A., Imane L., Hanae O., Abdelhay E. A., Fatima E. A., Lamya K., Abdelkarim O., Ahmed L., El Housseine R. Improved removal of methyl orange dye by adsorption using modified clay: Combined experimental study using surface response methodology. *Inorganic Chemistry Communications*. 2023, 155, 111127. https://doi.org/10.1016/j.inoche.2023.111127

[21] Urbain K. Y., Ollo K., Séverin E. N., Tchonrontcha K. Y., Albert T. Kinetic and Thermodynamic Study of the Elimination of Remazol Black on Activated Carbon Based on Ricinodendron Heudelotii Shells. *Journal of Materials Science and Chemical Engineering*. 2023, 11, 1-20. https://doi.org/10.4236/msce.2023.119001

[22] Khezami L., Capart R. Removal of Chromium (VI) from Aqueous Solution by Activated Carbons: Kinetic and Equilibrium Studies. *Journal of Hazardous Materials*. 2005, 123, 223-231. https://doi.org/10.1016/j.jhazmat.2005.04.012

[23] Fadi A. M., Bernard L. Effect of the adsorbate (Bromacil) equilibrium concentration in water on its adsorption on powdered activated carbon. Part 1. Equilibrium parameters. *Journal of Hazardous Materials*. 2009, 170(2-3), 744-753. https://doi.org/10.1016/j.jhazmat.2009.05.003