

Potential of a Tunisian Natural Clay to Remove Cationic and Anionic Dyes From Polluted Waters

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ABSTRACT

The objective of this study is to show the adsorption power of Tunisian smectitic clay from Jebel Aidoudi from the region of El Hamma (southern Tunisia). A cationic dye (Methylene Blue: MB) and an anionic dye (Orange II: OII) are used to determine the maximum absorbability of clay. Physico-chemical characterization tests (XRD, XRF, SBET) on the clay sample were performed. The experimental results showed that the optimal contact time of adsorption is 40 min (91.35% and 51.87%, respectively, for MB and OII). An increase in the retention rate of the dyes was noted by varying the adsorbent rate from 0.06 g to 0.12 g. The experimental results showed that the retention was strongly influenced by the pH of the medium (a high adsorption rate of MB at basic pH and a high adsorption rate for OII at acidic pH). The adsorption capacities are well described by the Langmuir isotherm. The pseudo-second order model is the most reliable for determining the order of adsorption kinetics of MM and OII by this smectitic clay.

INTRODUCTION

Organic dyes are mainly used in the textile and dyeing sector. These areas are among the most water consuming industries. They generate significant pollution because of the immense amounts of effluent generated, which is heavily loaded with acid or basic dyes [1]. Eliminating these kinds of pollutants is always a challenge. Numerous studies have developed several treatment processes in order to reduce the quantities of these contaminants in aquatic environments, such as adsorption, precipitation, membrane filtration, coagulation and chemical oxidation [2]. The

adsorption process is one of the methods that has shown great success for the elimination of contaminants of different kinds, in particular organic pollutants (pesticides, dyes, phenolic compounds, etc.) and heavy metals (cadmium, lead, mercury, etc.) [3]. In addition, the research and development of new naturally abundant adsorbents which are economically profitable and effective for the treatment of ecosystems is a great challenge [4,5]. Bioadsorbents such as biomass, solid agricultural waste and algae, and natural adsorbents such as soils and modified or unmodified clays have been shown to be promising materials for the trapping and removal of pollutants.

Adsorption on activated carbon is the most widely used and recommended process for the treatment of wastewater in industries. Despite its effectiveness, activated carbon remains an expensive material, and for the most part is imported, so finding new products that come from a cheap and locally available source is essential [6-8].

Clay minerals, in this case the smectite family, are among the materials most considered because of their well-known adsorption and pollutant retention properties as well as the possibility of their modification and/or functionalization [9-11].

The southern region of Tunisia is known for its vast clay deposits. In particular, clays of the smectite family, which are mainly used in the construction industry, and bentonite is applied as a waterproofing material and in the treatment of industrial effluents [12,13]. Clays are made up of minerals whose particles are essentially phyllosilicates. These form in sheets or layers, with intercalated metal ions between these layers. This type of structure leads to an interesting texture associated with very particular physicochemical characteristics, explaining the capacity of clays to allow numerous exchanges of cation and anion in the network [14,15]. In particular, smectitic clays typically consist of an anionic aluminosilicate sheet made of one tetrahedral layer topped by two or three octahedral layers, with a mobile layer of ionically attached metal cations separating these sheets.

The objective of this article is in two parts: as a first step, the physico-chemical characterization of a smectitic clay sampled from the southern region of Tunisia, and a second step, in which we studied the adsorption of cationic and anionic dyes chosen as organic pollutants (methylene blue and Orange II) by this clay. These studies were carried out as a function of several parameters in order to determine the optimal absorption conditions, and to contribute to the understanding of the behaviour of pollutant ions at the interface between clay particles and aqueous solutions.

MATERIALS AND METHODS

The clay sample (AD) used in this work was collected from the Southern Atlas region. A sample of lower Coniacian-Campanian age was taken from the Meider alternation formation in Jebel Aïdoudi (El Hamma region) (Figure 1).

Figure 1. Outcrops of the studied clay (AD).

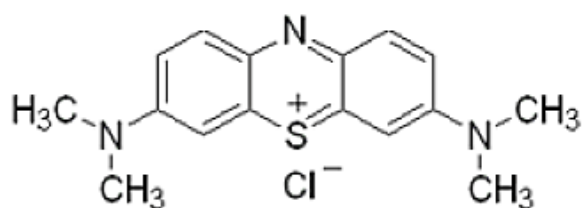


Methylene blue (MB) is a cationic dye, with the molecular formula $C_{16}H_{18}N_3SCl$, and a maximum absorbance at 663 nm. Orange II (OII) is an anionic dye, with the molecular formula $C_{16}H_{11}N_2NaO_4S$, and a maximum absorbance at 486 nm.

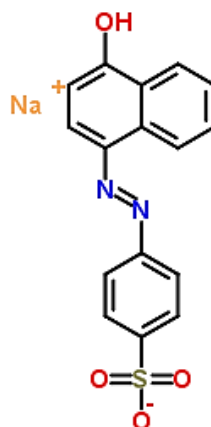
The structures of the two dyes are shown in Figure 2 (a) and (b), respectively.

Figure 2. Structures of (a) cationic dye methylene blue (MB) and (b) anionic dye Orange II (OII).

a.



b.



Characterisation of the clay

The determination of the mineralogical phases of our clay was carried out *via* X-Ray Diffraction (XRD) on a powder sample using an Philips Analytical X'PERT PRO diffractometer (with $CuK \alpha, \lambda=0.154056$ nm) [16]. The collected data ($10-80^\circ 2$ range, scan rate of $0.02^\circ/\text{min}$ (2)) were processed by Panalytical X'Pert Highscore software.

Chemical analysis was determined by X-ray fluorescence (XRF, Panalytical Axios Dispersive X-ray Fluorescence Spectrometer).

The specific surface area of the clay was determined from N_2 adsorption desorption isotherm at $-196^\circ C$ using the BET (Brunauer-Emmett-Teller) method. Sieved fractions under 150 microns in size were degassed for 72 h at $70^\circ C$ under high vacuum [17].

Adsorption experiments

For each experiment, the solid (clay) is brought into contact with a solution of distilled water in which the dyes have been dissolved.

For each dye (MB and OII), we treated identical volumes of the dye solution (100 ml) of initial concentration of 10 mg/l with a mass of 0.1 g of smectite clay. The mixture was stirred for one hour at room temperature ($25^\circ C$). Samples were collected at predetermined time intervals (0, 10, 20, 40, 60, 120 min) using a micropipette. The effect on the concentration of dyes was studied. The initial MB and OII dyes concentration chosen were: 10, 15, 20 and 25 ppm. The batch adsorption was performed in a thermostatic bath, by adding an amount of smectitic. We carry out the same procedure in a batch system, by adjusting the initial pH of the solutions of the dyes using the solutions of NaOH (1N) and HCl (1N), for the different pH values studied (3, 5, 7, 9 and 11). The adsorbate was then separated from the

adsorbent by centrifugation for 15 min at 3000 rpm. The concentration of MB and OII was determined by measuring the absorbance at maximum wavelengths (λ_{max} MB=663 nm, λ_{max} OII=486 nm) by UV-Vis spectrophotometry (Shimadzu UV3100).

The percentage degree of MB and OII adsorption was calculated using the following equation 1:

$$q_e = (C_0 - C_e) \times \frac{V}{m} \dots\dots\dots (1)$$

Where:

q_e is the capacity at adsorption equilibrium (mg/g);

C_0 is the initial concentration of the dye in the solution (mg/l);

C_e is the concentration of the dye in the solution (mg/l) at time t (t being the contact time);

V is the volume of methylene blue or orange dye II solution (ml);

m is the mass of clay (g).

Adsorption isotherms

Two commonly used models, Langmuir [18] and Freundlich [19], were selected (Table 1) to investigate the process of dye-clay interaction.

Table 1. Isotherm models: Langmuir and Freundlich.

Adsorption model	Langmuir	Freundlich
Non-linear form	$1/q_e = 1/q_m + 1/K_{Lqm}C_e$	$\log q_e = \log K_f + 1/n \log C_e$

Where: q_e is the amount of the solute at equilibrium (mg/g); C_e is the concentration of the equilibrium solute (mg/l); q_m is the amount of adsorption (mg/g); K_L is the Langmuir constant; K_f is the Freundlich constant which expresses the adsorption affinity (L mg⁻¹); $1/n$ is the Freundlich constant which reflects the intensity of adsorption.

Adsorption kinetics

In the present work, two kinetic models were selected to study the kinetic behaviour of pollutants on the clay (AD) surface, namely the pseudo-first order kinetic model and the pseudo-second order kinetic model.

The pseudo-first order kinetic model was proposed by Lagergren [20] and assumes that the adsorption rate at time t is proportional to the difference between the amount adsorbed at equilibrium and that at time t, as shown in equation 2:

$$\frac{dQ_t}{dt} = K1 (Q_e - Q_t) \dots\dots\dots (2)$$

Where:

Q_t : Quantity adsorbed at time t in mg/g;

Q_e : Amount adsorbed at equilibrium in mg/g;

T : contact time (min);

K_1 : First order rate constant (min^{-1});

After integration, equation (2) becomes equation 3:

$$\log (Q_e - Q_t) = \log Q_e - (K_1 / 2.303) t \dots\dots\dots (3)$$

The pseudo-second order kinetic model allows characterization of adsorption kinetics by assuming rapid adsorption of the solute at high-energy sites, and relatively slow adsorption at low energy sites.

The pseudo-second order kinetic model [21] is expressed according to the following equation:

$$\frac{dQ_t}{d_t} = K_2 (Q_e - Q_t)^2 \dots\dots\dots (4)$$

After integration, equation (4) becomes:

$$t / Q_t = 1 / K_2 Q_e^2 + 1 / Q_e \dots\dots\dots (5)$$

Where:

K_2 = adsorption rate constants for the pseudo-second order ($\text{g mol}^{-1} \text{min}^{-1}$).

Q_e = quantity of adsorbate at equilibrium per gram of adsorbent (mg/g).

RESULTS AND DISCUSSION

Characterization of studied clay

Mineralogical analysis shows that Jebel Aidoudi clay (AD, Table 2) contains, in addition to clay minerals, non-clay minerals mainly represented by quartz (5%), calcite (5%) and feldspar (1%). The mineralogy of the fraction less than 2 μm in diameter is essentially composed of mineral clays of the smectite (76%), kaolinite (9%) and illite (4%) type.

The chemical analysis of AD clay showed a dominance of SiO_2 (49.53%), Al_2O_3 (18.87%), and Fe_2O_3 (7.65%), as would be expected (Table 2). The loss on ignition (LOI) is 15.07% (Table 2).

Table 2. Mineralogical and chemical quantification of the smectitic clay sample (AD). LOI=Loss On Ignition.

Mineral phases	Weight (%)	Oxides	Weight (%)
Smectite	76	SiO_2	49.53
Illite	4	K_2O	1.49
Kaolinite	9	Al_2O_3	18.87
Calcite	5	Fe_2O_3	7.65
Quartz	5	Na_2O	1.83
Feldspars	1	P_2O_5	0.29
-	-	TiO_2	0.93

-	-	MnO	0.02
-	-	CaO	2.21
-	-	MgO	2.08
-	-	LOI	15.07

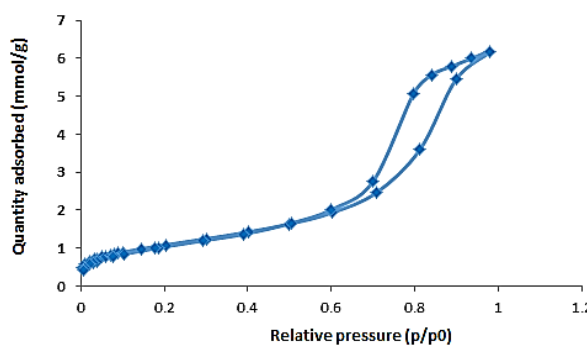
The characteristics of the porous structure of the AD clay sample are summarized in Table 3. The BET specific surface area of AD clay is around 84 m²/g due to the dominance of smectitic minerals. This value is close to that reported by Chaari et al., who studied this clay.

Table 3. Specific surface area, pore volume, and average pore diameter of studied clay, as determined by BET.

Sample	SBET (m ² /g)	Pore volume (cm ³ /g)	Pore diameter(Å)
	84	0.2	82

The nitrogen (N₂) adsorption isotherms of AD are shown in Figure 3. This type of isotherm is type IV (Figure 3), with the initial part of the isotherm being attributed to monolayer-multilayer adsorption, while the section containing hysteresis loop is associated with capillary condensation taking place in the mesopores. The shape of the hysteresis loop most closely resembles the Type H3 loop, which is typically observed with aggregates of plate-like particles, such as the layered sheets of clays, which give rise to slit-shaped pores [22]. Hence, this adsorbent is mesoporous (with a pore diameter exceeding 20 Å) [23]. The measured BET diameter of the pores of the clay was 82 Å.

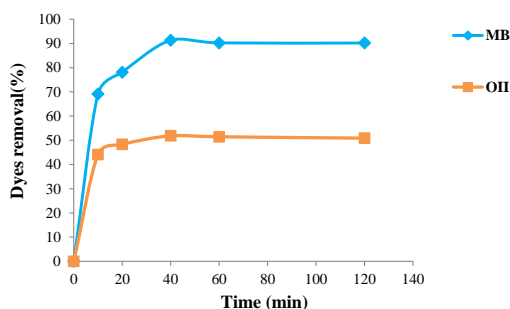
Figure 3. BET N₂ adsorption isotherm of the studied clay (AD).



Adsorption tests

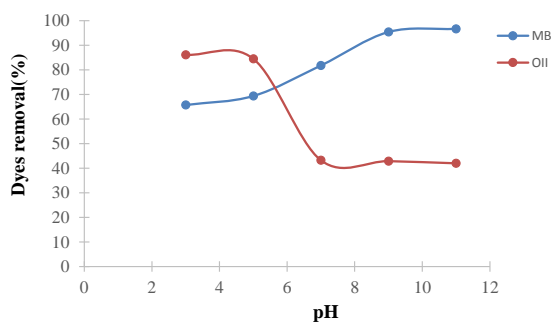
Effect of contact time: The results of the adsorption rate of MB and Oil dyes by AD clay as a function of contact time at non-adjusted pH are shown in Figure 4. The results showed that the adsorption capacity of MB and Oil dyes by the clay increases rapidly initially, up to a time of 60 min, and then remains almost constant beyond this period (rapid absorption, elimination after 40 min of 90% for MB and 51% for Oil). This low retention efficiency of the anionic dye Oil compared to the cationic dye MB can be explained by the greater difficulty for the smectic clay (anionic sheets intercalated with cations) to adsorb anionic dyes [24].

Figure 4. Effect of contact time on the adsorption of dyes (MB and OII) by the clay (AD) (madsorbent=0.1 g, Ci=10 ppm, T=25 °C, Time=120 min). **Note:** —◆— MB, —■— OII



Effect of pH: The pH plays an important role in the adsorption of the dyes studied, as shown in Figure 5. We can see from this figure that the adsorption capacity for the cationic dye MB is at a maximum at basic pH (97%). On the other hand, in the case of the anionic dye (OII), the retention was highest in an acidic medium (86%), and lower in a basic medium.

Figure 5. Effect of pH on the adsorption of dyes (MB and OII) by the clay (madsorbent=0.1 g, Ci=10 ppm, T=25 °C, pH=3, 5, 7, 9 and 11). **Note:** —●— MB, —●— OII



Several previous studies have been done on the adsorption of anionic dyes by clay. We can cite [1] who also showed that the optimum pH for adsorption of anionic dyes by smectitic clay was at an acidic pH.

This could be explained by the fact that in the acid state, the positive charge dominates the surface of the adsorbent. Thus, a significantly higher electrostatic attraction exists between the positive charges on the surface of the adsorbent and the negative charges on the dye [25,26].

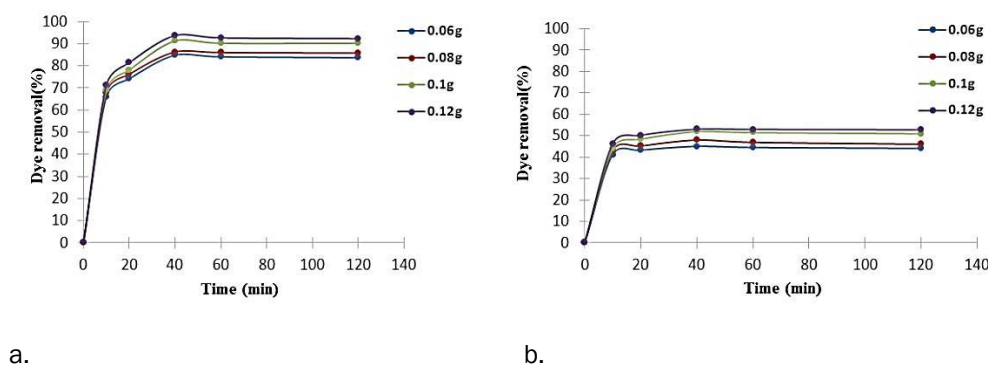
At basic pH, despite the presence of OH⁻ ions, we find that the capacity is higher compared to neutral pH 7, so we can say that there is always an attraction between the dyes and the adsorbent; there would be little competition between OH⁻ ions and anions in dyes at basic pH.

For the cationic MB dye the capacity for adsorption by the clay increases with increasing pH, up to pH 9, but then shows no further increase with pH increases.

Effect of adsorbent amount: It appears through the results presented in Figure 6, that for the dye concentration of 10 mg/l, and for a contact time of 120 minutes, an increase in the clay mass from 0.06 g to 0.012 g leads to an increase in the adsorption rate of MB of the order of 84% to 93%. Likewise for the anionic dye OII, by increasing the mass used,

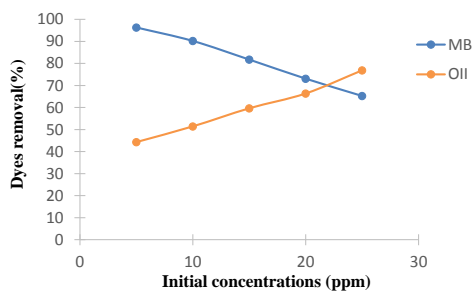
the adsorption rate goes from 45% to 53%. This can be explained by an increase in the number of possible binding sites on the surface of the adsorbent [27].

Figure 6. Effect of amount adsorbent (AD) on adsorption of a) MB and b) OII (Ci=10 ppm, T=25 °C, final time=120 min).**Note:** —●— 0.06 g, —●— 0.08 g, —●— 0.1 g, —●— 0.12 g



Effect of initial dye concentration: From the results presented in Figure 7, the clay adsorption capacity of the cationic dye decreases with increasing initial concentrations (96.34% using 5 ppm and 65.26% using 25 ppm). In contrast, the clay adsorption capacity of the anionic dye increases with increasing initial dye concentrations (44.32% using 5 ppm and 76.88% using 25 ppm). This means that the saturation level is not reached and that the clay could adsorb even larger amounts. It would have been necessary to increase the dye concentrations to define the saturation threshold of the clay [10].

Figure 7. Effect of initial concentration of MB and OII in dyes solution on adsorption of MB and OII (Ci=5, 10, 15, 20, 25 ppm, T=25 °C, madsorbent=0.1 g, Time of Equilibrium=60 min). **Note:** —●— MB, —●— OII



Adsorption isotherms: The results of the parameters characterizing the Langmuir and Freundlich models for the adsorption of MB and OII are summarized in Table 4. The values of the regression coefficients indicate that the adsorption process for both cationic (MB) and anionic (OII) dyes by AD clay can be well described by either of these two isotherm models of Langmuir and Freundlich, with linear regression coefficients $R^2=0.986-0.997$ for Langmuir (monolayer adsorption) and 0.996 for Freundlich (multilayer adsorption), with all R^2 values being very close to unity. Based on the Langmuir isotherm, the value of the MB adsorption capacity ($Q_m=72.45$ mg/g) obtained is considerably higher than the OII adsorption capacity ($Q_m=7.84$ mg/g). This support the observation that smectitic clays have a significantly higher retention capacity for cationic dyes than anionic dyes [4]. In this work, the values of the maximum adsorption capacities (Q_m) of our smectitic clay sample obtained for MB and OII are similar to those found for many

dyes in other previous works (Table 4), although lower than the values reported in ref [28] for cationic CV (Cristal Violet) and ref [29] for anionic MO (Methyl Orange).

Table 4. Adsorption isotherm parameters for MB and OII adsorption. Comparison of the maximum monolayer adsorption of various dyes onto clay, from this work and others previously published (see references below in the table).

Types	Cationic dyes				Anionic dyes			
	MB (present study)	CV	AR	BG	OII (present study)	MO	CR	RB5
-	-	[28]	[30]	[30]	-	[29]	[10]	[9]
Langmuir isotherm								
qm (mg/g)	72.45	86.54	60.4	76.9	7.84	62.34	11.03	12
K _L	0.124	-	-	-	0.312	-	-	-
R ₂	0.997	-	-	-	0.996	-	-	-
Freundlich isotherm								
K _f (L/g)	2.735	-	-	-	1.234	-	-	-
n	1.643	-	-	-	0.116	-	-	-
R ₂	0.986	-	-	-	0.996	-	-	-

Where: MB: Methylene Blue; CV: Cristal Violet; AR: Allura Red; BG: Brilliant Green; OII: Orange II; MO: Methyl Orange; CR: Congo Red; RB5: Reactive Black 5.

Adsorption kinetics: The results obtained by applying the pseudo-first and second order kinetic models are collated in Table 5. The results presented in this table show that the pseudo-second order model is the most applicable in the case of the adsorption of both cationic dye (MB) and anionic dye (OII) by the smectitic clay studied (AD), which has a correlation index (R²) higher than that obtained by the pseudo-first order kinetic model in both cases. Likewise, and from the adsorption values (Q_e) presented in Table 5, we note that the calculated values of Q_e by the pseudo-second order model are in good agreement with those obtained experimentally. This indicates that it is chemisorption. These results are comparable with other studies which have found that the adsorption kinetics of dyes on clay supports follow the pseudo-second order [31,32].

Table 5. Kinetic parameters for the adsorption of selected dyes (MB and OII) on clay.

Dyes	Pseudo-first-order			Q _e (exp)	Pseudo-second-order		
	k ₁ (min ⁻¹)	Q _e (mg/g)	R ²		k ₂ (g/mg.min)	Q _e (mg/g)	R ²
MB	-0.045	41.81	0.83	53.17	0.021	49.53	0.99
OII	-0.015	56.34	0.89	41.32	0.009	37.88	0.98

CONCLUSION

The experimental results of adsorption of MB and OII on smectitic clay showed that the absorbability depends on the nature of the dye (cationic or anionic). This smectitic clay has better cationic dye (MB) adsorption capability than for anionic dye (OII), adsorbing 90% of MB and 50% of OII (10 ppm solutions) after 40 minutes with unmodified solution

pH. The adsorption rate was influenced by the pH of the medium (high adsorption of MB in basic medium versus high adsorption for OII to acidic medium). The adsorption kinetics are in good agreement with the models of Langmuir and/or Freundlich, and a pseudo-second-order was shown to be the most likely process for the two dyes studied. According to the results found from this work, we can consider that the smectitic clay of Jebel Aidoudi of the Elhamma region of southern Tunisia is a good low cost natural adsorbent material with a great capacity to adsorb MB and OII from aqueous solutions.

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AUTHOR CONTRIBUTION

The authors equally contributed for the preparation of the manuscript.

AVAILABILITY STATEMENT OF DATA AND MATERIAL

The data and material are available within the manuscript.

ETHICS DECLARATIONS

This is the new work and submitted to any journal first time. The manuscript is prepared as the ethical standard.

CONFLICT OF INTEREST

No potential conflict of interest was reported by the authors.

CONSENT TO PARTICIPATE

Yes.

CONSENT FOR PUBLICATION

Yes.

REFERENCES

1. Chaari I, et al. Comparative study on adsorption of cationic and anionic dyes by smectite rich natural clays. *J of Mole Struc.* 2018; 2860: 31349-31358.
2. Lazaar K, et al. Efficiency of natural clay and titania P₂₅ composites in the decolouring of Methylene Blue (MB) from aqueous solutions: Dual adsorption and photocatalytic processes. *Arab J of Geo.* 2021;14:400.
3. Eloussaief M, et al. Efficiency of natural and acid-activated clays in the removal of Pb (II) from aqueous solutions. *J of Hazar Mater.* 2010;178:753-757.
4. Tsai WT, et al. Adsorption of acid dye onto activated carbons prepared from agricultural waste bagasse by ZnCl₂ activation. *Chemosphere.* 2001;45: 51-58.

5. Hajjaji W, et al. Effective removal of anionic and cationic dyes by kaolinite and TiO₂/kaolinite composites. *Clay Miner.* 2016;51:19-27.
6. Yu-Li YR, et al. Colour removal from dye wastewaters by adsorption using powdered activated carbon: Mass transfer studies. *J Chem Technol Biotechnol.* 1995;63:48-54.
7. Meshko V, et al. Adsorption of basic dyes on granular activated carbon and natural zeolite. *Water Res.* 2001;35:3357-3366.
8. Partlan E, et al. Adsorption kinetics of synthetic organic contaminants onto superfine powdered activated carbon. *Chemosphere.* 2020; 253:126-628.
9. Aguiar JE, et al. Improvement in the adsorption of anionic and cationic dyes from aqueous solutions: A comparative study using aluminum pillared clays and activated carbon. *Sepa Sci and Technol.* 2014; 49:741-751.
10. Tamimi M, et al. A study of the remove cationic and anionic dyes in aqueous solution by a new natural clay. *Inter J of Engi Techn and Mana Res.* 2018;5:64-74
11. Kausar A, et al. Dyes adsorption using clay and modified clay: A review. *J Mol Liq.* 2018;256:395-407.
12. Chang WZ, et al. Ageing and collapse of bentonite gels-effects of Li, Na, K and Cs ions. *Rheol Acta.* 2014;53:109-122.
13. Putro JN, et al. Investigation of heavy metal adsorption in binary system by nanocrystalline cellulose-bentonite nanocomposite: Improvement on extended Langmuir isotherm model. *Microporous Mesoporous Mater.* 2017; 246:166-177.
14. Neumann MG, et al. Influence of the layer charge and clay particle size on the interaction between the cationic dye methylene blue and clay in aqueous suspension. *J Colloid Interface Sci.* 2002;225:254-259.
15. Ozcan AS, et al. Adsorption of acid blue 193 from aqueous solutions onto BTMA-bentonite. *Colloids Surf A.* 2005;266:73-81.
16. Ali RM, et al. Potential of using green adsorbent of heavy metal removal from aqueous solutions: Ads kinetics, isotherm, thermodynamic, mechanism and economic analysis. *Ecol Eng.* 2016;91:317-332.
17. Brunauer S, et al. Adsorption of gases on multimolecular layers. *J Am Chem Soc.* 1938;60:309-319.
18. Langmuir I. The adsorption of gases on plane surfaces of glass, mica and platinum. *J Am Chem Soc.* 1918;40:1361-1408.
19. Frenudlich HMF. Uber die adsorption in Losungen. *J Phys Chem.* 1906;57:385-470.
20. Lagergren SK. About the theory of so-called adsorption of soluble substances. *K Vet Akad Handl.* 1898;24:1-39.
21. Bhattacharyya KG, et al. *Azadirachta indica* leaf powder as an effective biosorbent for dyes: A case study with aqueous Congo red solution. *Environ Manag.* 2004;71:217-229.
22. Sing KSW, et al. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. *Pure Appl Chem.* 1985;57:603-619.
23. Lazaar K, et al. Production of silica gel from Tunisian sands and its adsorptive properties. *J Afr Earth Sci.* 2017; 130:238-251.
24. Hajjaji W, et al. Natural portuguese clayey materials and derived TiO₂-containing composites used for decolouring methylene blue (MB) and orange II (OII) solutions. *Applied Clay Sci.* 2013;83:91-98.
25. Chaari I, et al. Adsorption of a textile dye "Indanthrene Blue RS (C.I. Vat Blue 4)" from aqueous solutions onto smectite-rich clayey rock. *J of Hazar Mater.* 2009;172:1623-1628.

26. Chaari I, et al. Interactions of the dye, C.I. direct orange 34 with natural clay. *J of Allo and Comp.* 2015; 647:720-727.
27. Karim AB, et al. Removal of basic dye "Methylene Blue" in aqueous solution by Saficlay. *J Water Sci.* 2010;23:375-388.
28. Hamza W, et al. Sono-assisted adsorption of cristal violet dye onto tunisian smectite clay: Characterization, kinetics and adsorption isotherms, ecotoxicol. *Environ Saf.* 2018;163:365-371.
29. Fernandes JV, et al. Adsorption of anionic dye on the acid-functionalized bentonite. *Mater.* 2020;13:3600.
30. Ullah R, et al. Modified clays as an efficient adsorbent for brilliant green, ethyl violet and allura red dyes: Kinetic and thermodynamic studies. *Pol J Environ Stud.* 2019;29:3831-3839.
31. Kooli F, et al. Removal enhancement of basic blue 41 by brick waste from an aqueous solution. *Arab J Chem.* 2015;8:333-342.
32. Chargui H, et al. Direct Orange 34 dye fixation by modified kaolin. *Clay Miner.* 2018;53:1-32.