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ADSORPTION OF QUINALIZARIN FROM NON AQUEOUS SOLUTION ONTO ACID ACTIVATED PALYGORSKITE

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Introduction

Aromatic compound constitute a major class of pollutants in waste waters from many industries. These compounds must be removed from waste-waters before they are discharged into the environment because of their high toxicological potential. Quinalizarin (1,2,5,8-Tetrahydroxy-antraquinone) is among such compounds. The major use of quinalizarin is in manufacture of dyes and pigments. The treatment of textile waste, comprising of dyestuffs and other non-biodegradable organics, poses considerable problems in the waste water treatment industry. It is difficult to remove this kind of waste because they are stable to light, heat and oxidizing agents and biologically non-degradable [1].

Adsorption is known to be one of the most promising processes of removing pollutant dyes from waste [2, 27, 3]. Activated carbon is the most widely used adsorbent for the removal of colour from textile effluents due to its high surface area and high adsorption capacity [4–6]. However it has a high cost and needs regeneration after each adsorption experiment. Recently, clay materials either as such or after modification, have been increasingly paid attention because they are cheaper; they have high specific surface area, high chemical stability and a variety of surface and structural properties [7–10]. To our knowledge, little attention was paid to fibrous clays even more, to acid activated fibrous clay. A limited number of studies were achieved using sepiolite as adsorbent [11–13] and palygorskite [14, 15].

The aim of this work is to study the adsorption of quinalizarin from organic solution onto acid activated palygorskite. Palygorskite was classed as a 2:1 layer inverted structure. Because of the inversions in the silica tetrahedral sheet, the structure has parallel channels or holes throughout, give a high surface area and a high capacity to adsorb and absorb various materials. Appropriate acid treatments modify its structural and textural properties and make it beneficial for many industrial applications (Environment absorbent, pharmaceuticals, catalyst support, petroleum refining, mineral and vegetable oil refining…).

Materials and methods

Adsorbent

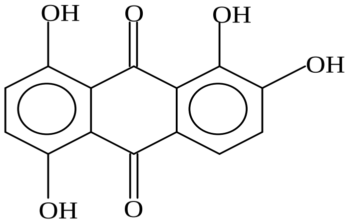
Red palygorskite from south Tunisia was used as starting material. The crude sample contains impurities mainly dolomite (8%, measured by calcimetry) and less than 5% of quartz. Crude palygorskite was firstly treated with dilute HCl solution in order to remove carbonate. Then, it was washed with distilled water by centrifugation and dialysis to remove excess chloride. After sedimentation, the purified fraction was dried and ground to less than 60 µm. Referring to ASTM file (Reference code: 21-0957), Tunisian palygorskite has monoclinic structure. Chemical composition of purified sample is SiO_2 53.5%, Al_2O_3 11.98%, MgO 12.05%, Fe_2O_3 5.9%, K_2O 0.72%, Na_2O 0.03%, CaO 0.09%, LOI 16% and its structural formula, calculated according to [16], is as follows:

$(Si_{7.324}Al_{0.676})(Mg_{2.459}Al_{1.257}Fe_{0.608})(K_{0.125}Na_{0.008}Ca_{0.013})O_{20}(OH)_2(H_2O)_4\ 4(H_2O)$

The cation exchange capacity (CEC) determined by Kjeldahl method is 23 meq/100g and its specific surface area is 59.7 m^2g^{-1}. The purified palygorskite sample was subjected to acid treatment with 2M hydrochloric acid using solid/liquid ratio of 1/10 (w/w) at boiling temperature under reflux for different periods. The resulting solids were washed with distilled water until chloride free and constant pH.

Adsorbate

The organic molecule dye used as adsorbate in this study is the 1,2,5,8-Tétrahydroxy- antraquinone (quinalizarin). Its molecular structure is given by the following chemical formula:



Methods

Activated and no activated palygorskite was characterised by X ray diffraction (using Pan analytical X'Pert High Score Plus diffractometer equipped with a Cu anticathode), Chemical analysis [17] and specific surface area (using Micrometric Autosorb 2050 Analyser) was determined from the nitrogen adsorption isotherms at 77 K by the BET method and after out degassing the samples at 150°C with the residual pressure of 10^{-5} mm Hg. Acid-base properties of different samples were determined using potentiometric titration [18].

The adsorbate concentration were analysed spectrophotometrically with UV-Visible spectrophotometer (Perkin Elmer Lomda 90) at 492 nm).

Adsorption experiment

Adsorption tests were carried out by mixing 0.1g of each adsorbent with 50ml of quinalizarin dissolved in ethanol. The initial quinalizarin concentration is ranged between 2.5 10^{-4} and 2.5 10^{-5} mol L^{-1}. The whole was shaken at 100 rpm at room temperature for 24h to ensure adsorption equilibrium. After the contact time was completed, the suspension was centrifuged at 4000 rpm for 15min. Quinalizarin remaining in the supernatant was analysed by spectophotometry at 492 nm. Adsorption isotherm is constructed by measuring the concentration of the adsorbate in the medium before and after adsorption using the following equation: $Q_{ads} = \frac{(C_0 - C_{eq})V}{m}$

Where Q_{ads} is the amount of quinalizarin adsorbed on palygorskite sample at considered equilibrium concentration (mol g^{-1}), C_0 the initial concentration of quinalizarin solution (mol L^{-1}), C_{eq} the equilibrium concentration of quinalizarin solution (mol L^{-1}), V the volume of quinalizarin solution (L) and m the mass of adsorbent used (g).

Results and discussion

Characterisation of the adsorbents

Acid treatment caused a progressive decrease in octahedral cations (Al, Mg and Fe) and a residual enrichment in SiO_2 (table 1). In the beginning of acid treatment, the decrease in octahedral cations is limited showing the resistance of palygorskite structure and the difficulties of the opening of the channels. Once the H^+ access throughout the structure is facilitated, the dissolution becomes rapid and reaches its maximum at 35h. For longer activation times, we note an increase in the octahedral cations, which can be attributed to coprecipitation.

Table 1. Chemical compositions of untreated and acid treated samples expressed in oxide form/100g of calcined sample

Samples	SiO_2	Fe_2O_3	MgO	Al_2O_3
Paly	63.69	7.023	14.34	14.26
Paly 2M8h	71.4	5.96	11.89	11.09
Paly 2M14h	73.33	5.59	11.38	10.06
Paly 2M35h	88.08	0.66	4.60	7.08
Paly 2M50h	79.58	3.79	5.76	8.57

The X-ray diffractograms of purified and acid treated samples are presented in fig. 1. The untreated palygorskite has sharp strong reflexions at 10.5, 6.4, 5.4, 4.5, 3.68 and 3.23Å. With increasing treating time, the crystallinity of palygorskite decreased, with a concomitant formation of amorphous utter. The latter can be observed by the appearance and increase of a broad ham at 16-30° 2θ. After 35h treatment only this ham is observed indicating the complete destruction of the clay.

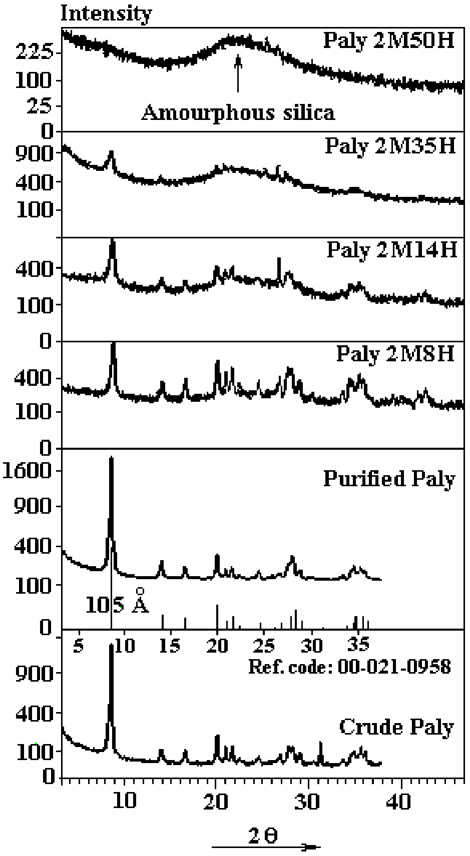


Fig. 1. XRD diffractograms of treated and untreated palygorskite

BET specific surface area gradually increases with treating time up to 35h (from 59.7 to 437 m^2g^{-1}) decreasing thereafter (table 2). Such behaviour has been observed in the past [19–21]. The initial increase of S_{BET} is attributed to the opening of the structure channels following dissolution of the octahedral sheet and amorphous silica formation; whereas the decrease can be attributed to the condensation of the silanol groups [26]. This confirms that silica contributes to the total amount of the surface area. Moreover, activation increases the total pore volume, from 0.3494 to 1.039 cm^3g^{-1}, due to development of mesoporosity.

Table. 2. Surface parameters of different palygorskite samples and maximum amount of adsorbed quinalizarin

Sample	S_{BET} (m^2g^{-1})	Vp (cm^3 g^{-1})	H_S (mmol g^{-1})	Ds *(sites nm^{-2})	Qmax (µmol g^{-1})
Paly	59.7	0.3494	0.518	5.22	1.8
Paly2M8h	161.6	0.5517	1.003	3.74	3.8
Paly2M14h	212,3	0.6118	1.012	2.87	3.56
Paly2M35h	437.0	1.0390	1.527	2.1	3.65
Paly2M50h	138.3	0.6631	1.425	6.2	2.5

$* Ds = \dfrac{(H_s \times N_A)10^{-3}}{S_{BET} \times 10^{18}}$ (sites nm^{-2}); Where: N_A is the Avogadro's number (6,02 .10^{23} mol^{-1})

The total surface site per solid weight (Hs) calculated from the potentiométric data by using the Gran plot in a previous work [22] is given on table 2. As expected, the Hs value increases with the period of acid activation. It passes from 0.518 $mmolg^{-1}$ in starting material to 1.53 $mmolg^{-1}$ in Paly 2M35h. Beyond this activation time, the total surface site decreases slightly.

The site density values (Ds) show that no correlation exists between the total surface site (Hs) and the surface site area S_{BET} (table 2).

Adsorption isotherms

To identify the mechanism of the adsorption process, the adsorption of quinalizarin onto palygorskite is determined as a function of equilibrium quinalizarin concentration (Ce) and the corresponding adsorption isotherms are plotted in fig. 2. According to the classification of [23], the isotherm seems to be of the L type, indicating that the quinalizarin has a high affinity for the palygorskite surface. All isotherms are similar in shape and they show two clear plateaus. Adsorption isotherms with two plateaus were also observed in some studies concerning the adsorption of organic molecules on silica surface [24] and a sulphate adsorption on a volcanic ash soil [25].

According to the results of the quinalizarin adsorption isotherm experiments, the modified palygorskites had higher adsorption capacities than the natural sample. It was believed that the surface structural changes of the material, play the most important role in the adsorption capacities of the quinalizarin. When the natural palygorskite sample was treated with 2M HCl, the surface structural of the material was changed due to the opening of channels, the creation of mesocroporosity and the increase of the surface acidity. However, no correlation of Qmax was observed nor with specific surface area, nor with the total surface site (Hs) (table 2).

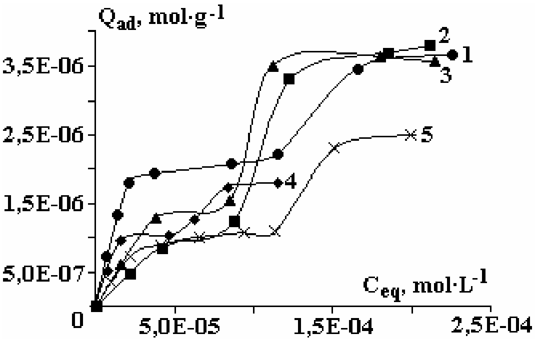


Fig. 2. Adsorption isotherms of quinalizarin onto palygorskite before and after acid activation

Modelling adsorption isotherms

The equilibrium adsorption isotherms are one of the most important data to understand the mechanism of the adsorption systems. Several isotherm equations can be used to explain solid/liquid adsorption system. The most commonly used are Langmiur and Freundlich isotherms. The Langmuir adsorption isotherm assumes that adsorption occurs at specific homogeneous sites within the adsorbent and has found successful application in many studies of monolayer adsorption. The linear form of the Langmuir isotherm equation is written as:

$$\frac{Ceq}{Qad} = \frac{1}{KQ_m} + \frac{1}{Q_m}Ceq$$

Where Qad is the equilibrium capacity of adsorbate on adsorbent (mol g^{-1}), Ceq is the equilibrium concentration of adsorbate solution (mol L^{-1}), *Q*m is the monolayer adsorption capacity of the adsorbent (mol g^{-1}), and K is the Langmuir adsorption constant (L mol^{-1}) and is related to the free energy of adsorption.

The Freundlich isotherm is an empirical equation employed to describe heterogeneous adsorption surface with sites that have different energies of adsorption and are not equally available. The Freundlich isotherm is more widely used but provides no information on the monolayer adsorption capacity, in contrast to the Langmuir model. Its linearized form can be written as follows: $LnQad = LnK_f + nLnCeq$

Where: K_f (L g^{-1}) and *n* (dimensionless) are the Freundlich adsorption isotherm constants, being indicative of the extent of adsorption and the degree of nonlinearity between solution concentration and adsorption, respectively.

The correlation coefficients, calculated from the linear Langmuir and Freundlich equations, show that the measured adsorption could not be fitted with these models (table 3).

Table 3. The correlation coefficients calculated from the linear Langmuir and Freundlich

	Langmuir	**Freundlich**
Paly	0,896	0,987
Paly 2M8h	0,32	0,837
Paly 2M14h	0,67	0,675
Paly 2M35h	0,892	0,840
Paly 2M50h	0,52	0,851

Based on this result and the isotherms shape we can suggest that the adsorption sites aren't homogenous but there are two kinds of adsorption sites: the stronger and the weaker sites. In order to check this hypothesis, we modified the Langmuir model as follows:

$$Qad = \frac{Q_{m_1}K_1C_{eq}}{1+K_1C_{eq}} + \frac{Q_{m_2}K_2C_{eq}}{1+K_2C_{eq}}$$

where Qm_1 , K_1 et Qm_2 , K_2 are respectively the Langmuir parameters for the stronger and weaker sites.

The modified Langmuir parameters for the adsorption of quinalizarin are listed in table 4. Results show regression coefficients close on the unity (0.941-0.998). The maxima of quinalizarin adsorption at the stronger (Qm_1) and the weaker adsorption sites (Qm_2) increase with the acid activation time up to 35h and decrease thereafter. The experimental data produced perfect fit with the modified Langmuir isotherm showing that the surface of palygorskite was non-uniform in nature (fig. 3).

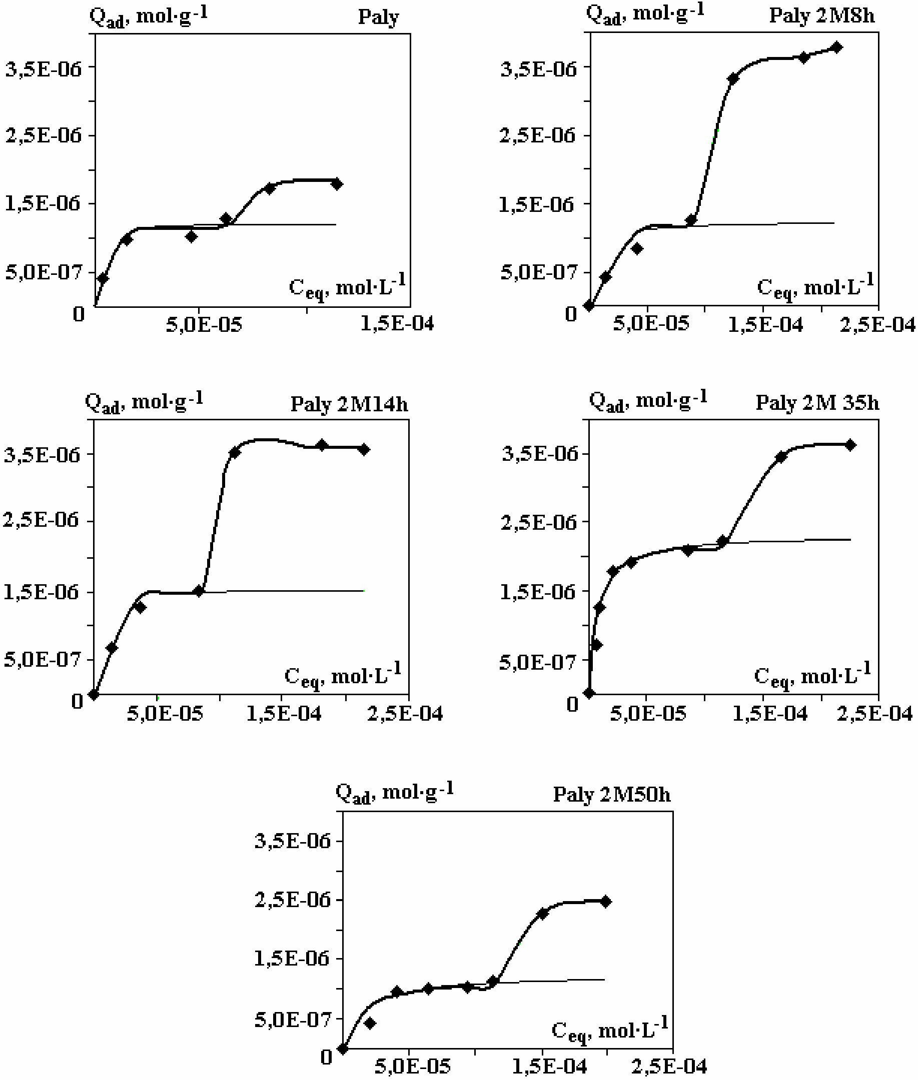


Fig. 3. The measured quinalizarin adsorption isotherms and the calculated Langmuir isotherms

Table 4. Langmuir isotherm constants and correlation coefficients. (1)for the stronger and (2) for weaker adsorption sites

	Paly	**Paly 2M8h**	**Paly 2M14h**	**Paly 2M 35h**	**Paly 2M50h**
R^2_1	0.974	0.988	0.998	0.995	0.941
Qm_1 µmol g^{-1}	1.23	1.25	1.54	2.32	1.23
K_1 L mol^{-1}	372136	160482	350391	139605	68072
R^2_2	0.998	0.987	0.992	0.997	0.995
Qm_2 µmol g^{-1}	1.00	2.73	2.12	2 .25	2.55
K_2 L mol^{-1}	16085	11723	181800	7232	5602
(Qm_1+Qm_2)µmol g^{-1}	2.23	3.98	3.66	4.57	3.78

The thin lines were obtained using the simple Langmuir equation at the stronger adsorption sites .The thick lines were obtained using the modified Langmuir equation.

Conclusion

Acid activation increases the adsorption capacity of palygorskite. Under the same conditions the Qmax value for HCl activated palygorskite was about twice larger than for the non treated palygorskite. This increase is the result of structural surface changes.

Using the measured and theoretical isotherms, two kinds of adsorption sites was suggested: stronger and weaker adsorption sites. This heterogeneity was checked by using the modified Langmuir model.

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Summary

In this study, the adsorption of quinalizarin by natural and mesoporous acid activated palygorskite has been examinated in order to remove coloured textile dyes from non aqueous solutions. The adsorption of quanilizarin from ethanol solution onto acid activated palygorskite was followed by UV-Visible measurement. The adsorption capacity was largely improved when the clay was activated by HCl. The high adsorption extents were observed from 2M8h to 2M 35h acid treated palygorskite samples. Adsorption isotherms of quinalizarin on acid activated palygorskite were determined and correlated with common isotherm equations such as Langmiur and Freundlich models. It was found that i/the adsorption isotherm exhibits two plateaus ii/ no model fit the isotherm data. In order to explain the adsorption behaviour of quinalizarin from ethanol onto palygorskite, the presence of stronger and weaker adsorption sites was suggested and checked by using the modified Langmuir model.